Research Progress on Graphene Oxide/Metal Oxide-Based Sonophotocatalytic Materials for the Degradation of Refractory Organic Pollutants

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Abstract: As an important branch of advanced oxidation processes (AOPs), sonophotocatalytic coupling technology demonstrates irreplaceable advantages in the deep treatment of refractory organic pollutants through the multi-dimensional synergy between ultrasonic cavitation and photocatalysis, and has become a frontier topic in environmental engineering. Graphene oxide (GO) serves as an ideal support for constructing high-performance sonophotocatalytic composites due to its ultrahigh specific surface area, excellent electron mobility, abundant surface oxygen-containing groups, and strong adsorption capacity. This paper systematically reviews the synergistic mechanisms of sonophotocatalytic systems, with emphasis on the preparation methods, microstructure regulation, and sonophotocatalytic degradation performance of typical metal oxide/GO composites, including NiO/GO and CuO/GO. The generation pathways of reactive oxygen species (ROS), the separation and migration of photogenerated electron-hole pairs, and the quantitative calculation of synergy factors are thoroughly discussed. Studies show that the combination of GO with NiO, CuO, and other metal oxides effectively suppresses the recombination of photogenerated carriers via interfacial interactions, enhances mass transfer at the solid-liquid interface, and significantly improves the degradation efficiency and cycling stability toward typical refractory organic dyes such as rhodamine B and methyl orange. Finally, the existing challenges in the practical application of GO/metal oxide-based sonophotocatalytic materials are analyzed, and future development directions are prospected from the perspectives of material design, mechanism research, and process optimization. This review aims to provide theoretical guidance and experimental references for the rational design, controllable synthesis, and engineering application of high-efficiency sonophotocatalysts.

Keywords: Sonophotocatalysis; Graphene Oxide; Metal Oxide; Refractory Organic Pollutants; Synergistic Effect; Reactive Oxygen Species

1. Introduction

Rapid industrialization and urbanization have led to the continuous discharge of large amounts of refractory organic pollutants, including dyes, phenols, antibiotics, and pesticides, into the aquatic environment. These pollutants exhibit high chemical stability, poor biodegradability, strong toxicity, and high bioaccumulation potential, posing severe threats to global water security and ecological balance, and bringing great challenges to drinking water safety. Traditional water treatment methods show obvious limitations: biodegradation is inefficient and incomplete due to pollutant toxicity; physical adsorption only transfers pollutants without mineralization, easily causing secondary pollution; chemical precipitation is less effective for dissolved organics and costly. Therefore, developing efficient, economical, and environmentally friendly water treatment technologies for the deep mineralization of refractory organics has become an urgent task in environmental science and engineering.

Advanced oxidation processes can generate highly reactive oxygen species (e.g., $\cdot OH$, $\cdot O_2^-$, $^1O_2$) that completely mineralize organic pollutants into CO_2, H_2O, and inorganic ions. As an emerging AOP, sonophotocatalysis integrates the high selectivity of photocatalysis and the strong oxidation of ultrasonic cavitation. This synergistic system overcomes the drawbacks of single photocatalysis (high carrier recombination, low visible-light utilization) and single sonocatalysis (limited oxidation efficiency, high energy consumption), showing great potential in treating refractory organic pollutants[1].

Graphene oxide, a typical two-dimensional carbon nanomaterial, possesses ultrahigh specific surface area, abundant surface functional groups (hydroxyl, carboxyl, epoxy), superior electrical conductivity, and high chemical stability, making it an excellent catalyst support[2]. Compositing GO with metal oxides such as NiO and CuO improves the dispersion of nanoparticles, inhibits agglomeration, accelerates the transfer of photogenerated electrons, reduces electron-hole recombination, and enriches pollutants near the catalyst surface via strong adsorption[3]. In recent years, GO/metal oxide nanocomposites have attracted extensive attention in sonophotocatalytic degradation[4]. Based on recent advances, this review summarizes the synergistic mechanisms, preparation strategies, structural characteristics, and structure-activity relationships of GO/metal oxide sonophotocatalysts, analyzes current challenges, and proposes future perspectives[4].

2. Synergistic Mechanism of Sonophotocatalysis

The high efficiency of sonophotocatalysis arises from the multi-dimensional synergy between ultrasonic cavitation and photocatalysis, rather than simple superposition[1]. The core mechanisms include ROS superposition, enhanced carrier separation, refreshed active sites, and improved interfacial mass transfer[1,5-6]

2.1 Ultrasonic Cavitation

Ultrasonic cavitation involves the formation, growth, and violent collapse of microbubbles in liquids under ultrasonic irradiation. At the moment of collapse, local high temperature (4000-5000 K) and high pressure (100-500 atm) are generated, accompanied by strong shockwaves and microjets. Under such extreme conditions, water and organic molecules undergo pyrolysis to produce $\cdot OH$ and other ROS, directly degrading pollutants. Meanwhile, shockwaves and microjets reduce catalyst agglomeration, remove intermediates from the surface, maintain active sites, and enhance mass transfer between the bulk solution and catalyst surface[1,7-8].

2.2 Photocatalytic Principle

When a semiconductor catalyst is irradiated by photons with energy greater than its band gap, electrons (e^-) are excited from the valence band (VB) to the conduction band (CB), leaving holes (h^+) in the VB. Photogenerated h^+ directly oxidizes organics or reacts with H_2O/OH^- to form $\cdot OH$. Photogenerated e^- reacts with O_2 to generate $\cdot O_2^-$, which further converts into H_2O_2 and $\cdot OH$. These ROS mineralize organic pollutants efficiently. The key to high photocatalytic activity is suppressing the recombination of e^--h^+ pairs[9-11].

2.3 Sonophotocatalytic Synergy

The synergy between ultrasound and photocatalysis significantly boosts degradation efficiency[1]:

1) ROS Superposition: Ultrasound and photocatalysis generate ROS through different pathways, greatly increasing the overall ROS concentration[1,12]

2) Carrier Separation Enhancement: Ultrasonic perturbation inhibits e^--h^+ recombination and prolongs carrier lifetime[1,5-6].

3) Active Site Renewal: Ultrasonic scouring removes adsorbed intermediates and keeps active sites exposed[1,7-8].

4) Mass Transfer Enhancement: Ultrasound reduces diffusion resistance and accelerates pollutant adsorption and product desorption[1,5].

Many studies confirm that the synergy factor of sonophotocatalysis exceeds 1.5, indicating strong positive synergy[1,3,6,8,10].

3. Functions of Graphene Oxide in Sonophotocatalysis

GO plays multifunctional roles in GO/metal oxide sonophotocatalysts[2]:

- Electron Transfer Highway: GO’s two-dimensional structure provides fast channels for photoelectrons, promoting e^--h^+ separation[2-3,8].
- Adsorption Enrichment: Large specific surface area and oxygenated groups strongly adsorb organic pollutants, increasing local concentration[2,11].
- Nanoparticle Dispersion: GO prevents metal oxide agglomeration and increases active sites via interfacial bonding[2-3,8].
- Visible-Light Response: GO extends light absorption to the visible region and narrows the

band gap of composites[2,9-10].
- Ultrasound Compatibility: GO maintains good dispersion under ultrasound and promotes cavitation-induced ROS generation[2,7-8].

Studies show that GO can increase the sonophotocatalytic efficiency of metal oxides by 2-10 times[2,13].

4. Conclusion

Sonophotocatalysis is a highly efficient AOP for refractory organic pollutants [1,4]. GO acts as an excellent support in GO/metal oxide composites, enhancing carrier separation, adsorption, visible-light response, and structural stability [2]. NiO/GO and CuO/GO show outstanding sonophotocatalytic activity and reusability for dye degradation [3,8]. The synergy between ultrasound, photocatalysis, and GO-based composites greatly improves catalytic performance [1,2,4].

5. Prospect

Although the research on GO/metal oxide-based sonophotocatalytic materials has achieved remarkable progress in recent years, there are still many key challenges to be solved for their practical engineering application in water pollution control [4]. The future development of this field will focus on the multi-dimensional optimization and innovation of materials, mechanisms and processes, and realize the transformation from laboratory research to practical application step by step. On the material design side, it is necessary to develop multi-component composite systems and introduce magnetic components into GO/metal oxide composites to realize the rapid separation and recycling of catalysts from the reaction system, which can not only reduce the material loss and use cost, but also avoid the secondary pollution caused by the catalyst residue [2,13]. In the aspect of mechanism research, it is urgent to combine in-situ characterization technologies and density functional theory (DFT) calculations to deeply reveal the microscopic interfacial interaction mechanism between GO and metal oxides, the migration and transformation law of photogenerated carriers in the composite system, and the generation and action mechanism of ROS under the combined action of ultrasound and light, so as to provide a more rigorous theoretical basis for the rational design of high-performance sonophotocatalysts [4-6]. For practical application verification, it is necessary to carry out degradation experiments on actual refractory organic wastewater instead of only using simulated dye solutions, and carry out pilot and industrial scale-up tests on the basis of laboratory research to explore the adaptability and stability of the material and technology in the actual water treatment process [4]. In the preparation process of materials, it is necessary to develop green, low-cost and scalable synthesis methods, abandon the traditional preparation process with high energy consumption and heavy pollution, and realize the large-scale and green preparation of GO/metal oxide composites, which is the key to reducing the application cost and promoting industrialization [3,8]. In addition, the exploration of multi-technology coupling systems such as sono-photo-Fenton and sono-photo-ozone will be an important development direction, and the immobilization of GO/metal oxide catalysts will also solve the problems of catalyst dispersion and recovery in the continuous reaction process, further optimize the sonophotocatalytic reaction process, and improve the treatment efficiency and practical application value of the technology [1,4]. With the in-depth development of the above research directions, GO/metal oxide-based sonophotocatalytic materials will break through the current application bottlenecks and play an increasingly important core role in the field of industrial refractory organic wastewater treatment and global water pollution control [2,4].

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