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Study on the Photocatalytic Properties of ZnO Nanorods rown on ITO Conductive lass

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Abstract: This study addresses the remediation of structural pollution in water bodies by exploring environmentally friendly pathways for water pollution degradation. Vertically oriented ZnO nanorod arrays were successfully fabricated on conductive glass substrates via a hydrothermal method. Utilizing these arrays as photocatalytic materials, efficient degradation of organic pollutants was achieved under solar irradiation. Scanning electron microscopy (SEM) characterization revealed that the fabricated ZnO nanorod arrays exhibit uniform density. The nanorods adopt a hexagonal prismatic structure, growing vertically on the substrate surface to form a highly porous structure with a large specific surface area. This morphology facilitates pollutant adsorption and enhances photocatalytic reaction efficiency. In photocatalytic performance testing, the ZnO nanorod array demonstrated outstanding degradation capabilities for two typical organic dye pollutants, methylene blue and rhodamine B. Under simulated sunlight irradiation, after a certain reaction time, its degradation efficiency for methylene blue reached 98.4%, while that for rhodamine B achieved 78%. These results conclusively demonstrate the prepared materials robust photocatalytic activity within the visible light spectrum. This study provides a viable material system and experimental basis for developing highly efficient, stable semiconductor photocatalysts and applying them to the treatment of refractory organic pollutants in water bodies.

Keywords: ZnO nanorods; SEM; Methylene blue; Rhodamine B.

1. Introduction

Currently, driven by robust policy initiatives and supported by technological innovation, water resources management is progressing toward sustainability. However, deep-seated challenges such as regional shortages, structural pollution, and ecological restoration require sustained long-term efforts [1-4]. Photocatalytic degradation of pollutants has garnered extensive attention due to its ability to efficiently break down contaminants in water while harnessing light energy-particularly solar energy-to directly decompose recalcitrant organic pollutants (such as dyes, pesticides, and pharmaceutical residues). This process mineralizes them into harmless small molecules like CO2 and H2O, achieving thorough treatment.

Photocatalysis offers the following significant advantages in improving water resource environments: First, they possess strong oxidizing power and broad-spectrum efficacy. The hydroxyl radicals (·OH) generated exhibit extremely high oxidation potential, enabling non-selective attack on various pollutants while also effectively inactivating microorganisms such as bacteria and viruses. Second, they are environmentally friendly and safe. The reaction process typically requires no addition of harmful chemicals, yielding clean end products and avoiding secondary pollution (such as sludge or toxic byproducts) that may result from traditional chemical treatments. Photocatalytic reactions occur under mild conditions, typically at ambient temperature and pressure. Energy consumption primarily stems from the light source (which can directly utilize sunlight), and operation is relatively straightforward. Furthermore, it can be powered by the vast potential of solar energy. Catalysts matched to the solar spectrum (such as modified visible-light catalysts) can directly harness abundant solar energy, providing sustainable, low-cost solutions for remote areas or distributed water treatment [5–7].

The core value of photocatalysis lies in providing a green, sustainable supplement or alternative to address the bottlenecks of traditional water treatment technologies, such as the low efficiency of biological methods in treating refractory organic compounds and the high chemical costs and residuals associated with advanced oxidation processes. It is particularly suitable for advanced treatment, removal of trace toxic pollutants, and safe disinfection of drinking water. Challenges and prospects for photocatalysis include: Practical large-scale application still faces engineering hurdles such as catalyst efficiency, stability, recyclability, and solar energy conversion efficiency. However, with continuous breakthroughs in novel catalysts (e.g., Z-type heterojunctions, single-atom catalysts) and reactor designs, it holds promising prospects in decentralized water treatment, emergency water purification, and integration with aquatic ecosystem restoration.

ZnO, as an outstanding photocatalytic material, has long been a significant research focus in the field of photocatalysis. It exhibits outstanding optoelectronic properties, with a bandgap width of approximately 3.37 eV, similar to TiO2, enabling efficient absorption of ultraviolet light and generation of photo-generated electrons and holes with strong redox capabilities. Its potent oxidative capacity, characterized by high oxidation potential of photo-generated holes, facilitates efficient degradation of various organic pollutants, certain inorganic substances, and microbial inactivation. ZnO is cost-effective and environmentally friendly, featuring abundant raw materials, low preparation costs, and inherent non-toxicity without secondary environmental pollution. Its morphology and structure are controllable, allowing synthesis of diverse nanostructures like nanorods, nanowires, and nanosheets through various methods. The large specific surface area enhances photocatalytic activity. Its high electron

mobility, significantly exceeding that of TiO2, facilitates rapid separation and transport of photogenerated carriers, minimizing recombination.

This study focuses on the growth of ZnO nanorods on conductive glass and analyzes the degradation performance of ZnO under both light-exposed and non-light-exposed conditions. Using the degradation of methylene blue and Rhodamine B as examples, the amount of pollutants present in water at different time points was analyzed to evaluate the materials degradation performance. Measurement data were obtained from the absorbance values recorded by a spectrophotometer.

Place the material prepared on a conductive glass substrate into a 100 ml dye solution containing 4 mg/L. Remove the solution at regular intervals, centrifuge to obtain the supernatant, and measure the absorbance. The degradation rate is calculated using the formula: y=(C0-Ct)/C0×100%=(A0-At)/A0×100%.

2. Experimental strategies

The experimental reagents used included: zinc acetate dihydrate (Zn (CH3COO)2·2H2O, Chengdu Kelong Chemical Co., Ltd.), anhydrous ethanol (C2H5OH, Chengdu Haixing Chemical Reagent Factory), zinc nitrate hexahydrate (Zn (NO3)2·6H2O, Tianjin Damiao Chemical Reagent Co., Ltd.), methylene blue (MB) dye, and rhodamine B (RhB) dye, both purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. The reaction vessel used was a high-pressure reactor. The prepared materials were characterized by SEM analysis.

3. Results and discussion

Figure 1 shows the surface morphology of the ZnO nanorod array film observed using a scanning electron microscope at a magnification of 2μm. The image clearly reveals that the conductive glass substrate surface is uniformly and densely covered by a large number of ZnO nanorods, forming a continuous thin film. These nanorods exhibit highly consistent vertical alignment on the substrate, arranged in an orderly fashion, demonstrating distinct array characteristics. Further observation reveals that ZnO nanorods exhibit well-defined outlines with a distinct hexagonal prismatic geometry, smooth side surfaces, and a relatively uniform diameter distribution, which indicate the excellent crystallinity of the nanorods. More importantly, the SEM images clearly reveal a strong preferential orientation growth characteristic of ZnO nanorods. The vast majority of nanorods grow perpendicular to the substrate plane, with a pronounced c-axis orientation. This highly ordered vertical arrangement typically stems from the preferential growth kinetics of crystals on specific crystal planes during hydrothermal growth, which is crucial for fabricating high-quality one-dimensional nanostructures. This uniformly coated, sharply defined, and highly oriented nanorod array structure endows the material with an exceptionally large specific surface area, favoring the increase in reactive sites. Simultaneously, the vertically aligned nanostructure provides efficient pathways for rapid, directional transport of photogenerated carriers, reducing their recombination probability. This morphological feature analysis provides a microstructural explanation for the outstanding performance exhibited by the material in subsequent photocatalytic experiments.

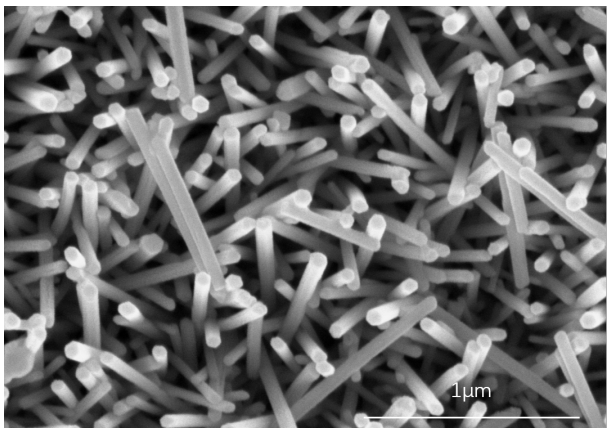

Figure 1. SEM image of ZnO nanorods

To systematically evaluate the photocatalytic performance of the prepared ZnO nanorod arrays, the organic dyes including methylene blue MB and RhB are employed as the target pollutant. Comparative degradation experiments were conducted under simulated sunlight irradiation and complete darkness conditions. The simulated sunlight was provided by a 300W xenon lamp, and the darkness conditions were achieved through light-blocking treatment. During the experiments, the degradated organic dye aqueous solution were periodically collected and analyzed using a UV-visible spectrophotometer to measure the solution absorbance at characteristic absorption wavelengths, thereby calculating concentration changes and degradation rates. Figure 2 displays the degradation curves of MB under both conditions. It clearly shows that MB concentration rapidly decreased with prolonged exposure time under simulated sunlight irradiation, exhibiting a typical exponential decay trend. After 90 min, the degradation rate reached 98.4%, indicating that ZnO nanorods can achieve near-complete removal of the pollutant under simulated sunlight irradiation. In stark contrast, under dark conditions, the degradation rate of MB is merely 9.1%. The minor degradation was primarily attributed to the physical adsorption of MB molecules on the ZnO nanorod surfaces. The stark difference in degradation rates between the two situations strongly confirms the dominant role of photocatalysis: light irradiation is the key condition for exciting ZnO to generate photo-generated electron-hole pairs. These photo-generated electrons and holes can further react with surface-adsorbed H2O or O2 to produce highly reactive species like ·OH and superoxide radical ($\cdot O_2^-$), thereby efficiently degrading MB molecules. In addition, the extremely low degradation rate under dark conditions further evidences that the photodegradation plays a crucial role in photocatalytic degradation. Thus, this comparative experiment clearly validates the outstanding photocatalytic activity of the prepared ZnO nanorod arrays, demonstrating promising application prospects for solar-driven water pollution treatment.

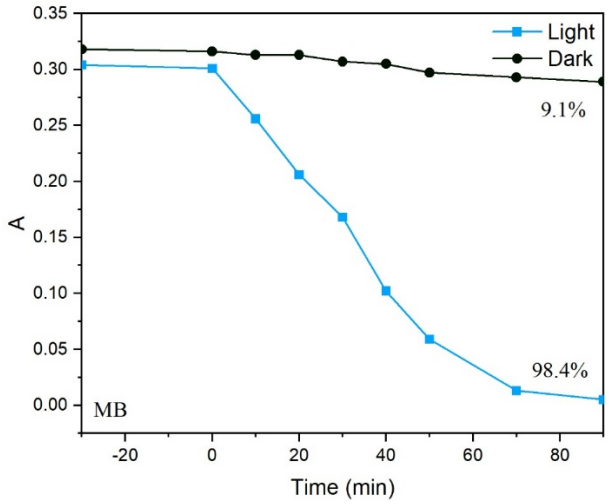

Figure 2. Degradation of MB by ZnO Nanorods

Figure 3 shows the degradation curve for RhB. Under light irradiation, the degradation of RhB by ZnO nanorods proceeds more slowly than that of MB, yet its photocatalytic degradation rate still reaches 78% after 90 min. In the absence of light irradiation, the degradation rate drops to only 9.6%. The underlying reasons is consistent with the photocatalytic degradation of MB.

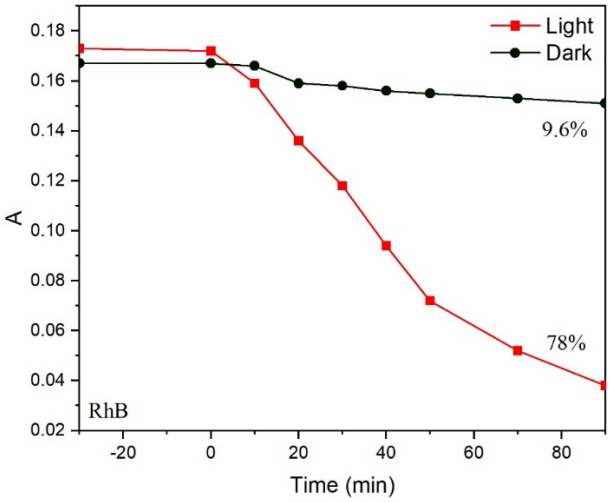

Figure 3. Degradation of RhB by ZnO Nanorods

Figure 4 illustrates the schematic of the reaction mechanism for the photocatalytic degradation of organic pollutants by the prepared ZnO nanorod array. When ZnO nanorods exposed to the light with energy (hv) exceeding its bandgap width (Eg), electrons (e^-) in the valence band (VB) are excited and jump to the conduction band (CB), the positively charged holes (h^+) are formed in the valence band, and thus generating a great deal of photo-generated electrons and holes. If these photogenerated charges rapidly separate and migrate to the ZnO nanorod surfaces, they can drive a series of redox reactions. Photogenerated holes migrating to the surfaces possess a strong oxidizing power, which are capable of directly oxidizing pollutant molecules or reacting with H2O molecules to generate ·OH with higher oxidative capacity. Simultaneously, the photogenerated electrons in the conduction band can react with adsorbed oxygen molecules on the nanorod surfaces, gradually generating $\cdot O_2^-$. These highly reactive radicals (·OH and $\cdot O_2^-$) can indiscriminately attack and cleave organic pollutants (such as MB and RhB), ultimately mineralizing them into small inorganic molecules like CO2, H2O and low-molecular-mass organic groups (LOGs) with no toxicity or microtoxicity [8].

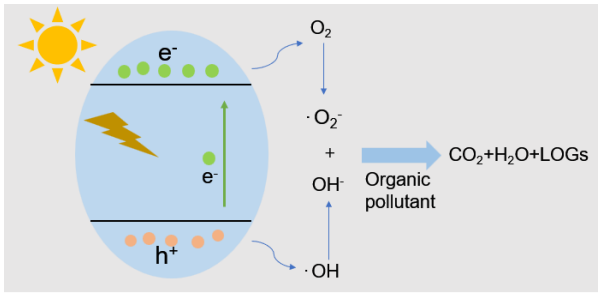

Figure 4. Schematic of the degradation mechanism of dyes by ZnO nanorods

4. Conclusion

ZnO nanorods prepared on ITO conductive glass exhibit uniform alignment and well-defined contours, demonstrating highly efficient degradation of MB and RhB dyes under simulated sunlight irradiation. The degradation efficiencies with light irradiation are 10 times and 8 times higher than those without light irradiation, respectively. The enhanced degradation efficiencies are attributed to the formation of a large number of photogenerated electrons and holes in the semiconductor materials under light exposure, increasing the active species (h^+, ·OH and $\cdot O_2^-$) participating in the surface oxidation reactions of the organic pollutant molecules.

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