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Preparation and Properties of Hollow TiO_2 Nanospheres

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Abstract: To address the issues of narrow photoresponse range, rapid carrier recombination, and difficulty in recovery associated with TiO_2 photocatalytic materials, this study employed a morphology control strategy to fabricate hollow spherical TiO_2 structures. By optimizing the microstructure of the hollow spheres, the aim was to broaden the light absorption range, increase the specific surface area, and enhance carrier separation. The photocatalytic degradation performance of the prepared material toward Rhodamine B aqueous solution-a typical organic pollutant-was experimentally evaluated, and its enhancement mechanism was explored. This work provides a feasible approach for designing efficient and easily recoverable TiO_2 photocatalysts.

Keywords: TiO_2, Rhodamine B, hollow spherical structure, morphology control.

1. Introduction

The rapid advancement of global industrialization and urbanization has led to increasingly prominent environmental pollution and energy crises, which have become two core challenges restricting the sustainable development of human society. Among these, the continuous accumulation of organic pollutants (e.g., dyes, pesticides, antibiotics) in water bodies poses a significant threat to ecological systems and human health. Semiconductor photocatalysis, as a green and efficient advanced oxidation technology, enables the mineralization of organic pollutants under ambient conditions via photogenerated reactive species. Owing to its notable advantages, including low energy consumption, no secondary pollution, and the capability to utilize solar energy, this technology has garnered extensive attention in the field of environmental remediation.

Titanium dioxide (TiO_2) stands out among semiconductor photocatalytic materials due to its high chemical stability, strong oxidation ability, non-toxicity, low cost, and favorable biocompatibility, thereby becoming the most studied and widely applied benchmark material in this field [1]. Since Fujishima and Honda discovered in 1972 that TiO_2 photocatalytic electrodes could decompose water under ultraviolet light, TiO_2 has demonstrated broad application prospects in environmental purification, solar energy conversion, self-cleaning coatings, and gas sensors [2].

In practical applications, the performance of TiO_2 is constrained by two key issues. First, owing to its wide bandgap (approximately 3.2 eV for the anatase phase), TiO_2 can only respond to ultraviolet light with wavelengths below 387 nm, and UV light accounts for only 4–5% of the solar spectrum, which severely limits its solar energy utilization efficiency [3]. Second, the rapid recombination of photogenerated electron–hole pairs (typically occurring on a picosecond to nanosecond timescale) severely restricts its quantum efficiency. Furthermore, conventional TiO_2 nanoparticles tend to agglomerate in liquid-phase reactions and are difficult to separate and recover, which further hinders their practical application.

To overcome these limitations, various modification strategies have been developed, including elemental doping, morphology control, surface sensitization, and heterojunction construction. Among these, morphology control, as an effective modification approach, can optimize the light absorption characteristics, specific surface area, and charge carrier transport pathways of TiO_2 by tuning its microstructure. Among various morphological architectures, hollow spherical structures have attracted considerable attention due to their unique geometric features and physicochemical properties [4].

2. Experimental

The preparation procedure for nano-TiO_2 microspheres is as follows. Ethanol and acetonitrile were added to a beaker and mixed homogeneously under magnetic stirring. Subsequently, aqueous ammonia and deionized water were added dropwise slowly, and the mixture was stirred for 10 minutes to ensure dispersion. Then, dibutyl titanate was introduced, and the reaction mixture was vigorously stirred at room temperature for 6 hours, resulting in the formation of a white suspension. Finally, the suspension was subjected to high-speed centrifugation. The obtained precipitate was washed repeatedly with ethanol and deionized water, and then dried in an oven at 60 °C.

The as-prepared nano-TiO_2 microspheres were dispersed in distilled water and ultrasonicated for 10 minutes. Thereafter, NaF and PVP were added, and the suspension was stirred at room temperature for 3 hours. The suspension was then transferred into a 100 mL polytetrafluoroethylene (PTFE) autoclave and subjected to hydrothermal treatment at 110 °C for 4 hours. After cooling to room temperature, the precipitate was collected, washed repeatedly with ethanol and deionized water, and dried under vacuum at 60 °C for 12 hours. The dried product was ground and subsequently calcined in a muffle furnace at various temperatures for 2 hours.

3. Results and Discussion

3.1. Microstructural Analysis

To comprehensively investigate the microstructural characteristics of the nano-TiO_2 hollow spheres, the surface

morphology and microstructure of the samples were systematically characterized using scanning electron microscopy (SEM). Figure 1 presents the SEM image of the as-prepared nano-TiO_2 hollow spheres. It is observed that the samples exhibit a uniform hollow spherical morphology with distinct interior cavities. Such a hollow architecture facilitates multiple reflections and scattering of light, thereby enhancing the light absorption efficiency.

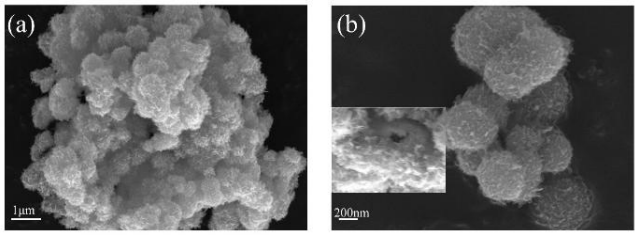

Figure 1. SEM images of the as-prepared nano-TiO_2 hollow spheres at different magnifications

To verify the successful synthesis of the nano-TiO_2 hollow spheres, elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS), as presented in Figure 2. As shown in Figure 2(b), the presence of Ti and O elements in the nano-TiO_2 hollow spheres was confirmed, and both elements were uniformly distributed. These results clearly demonstrate the successful fabrication of the TiO_2 hollow spherical architecture.

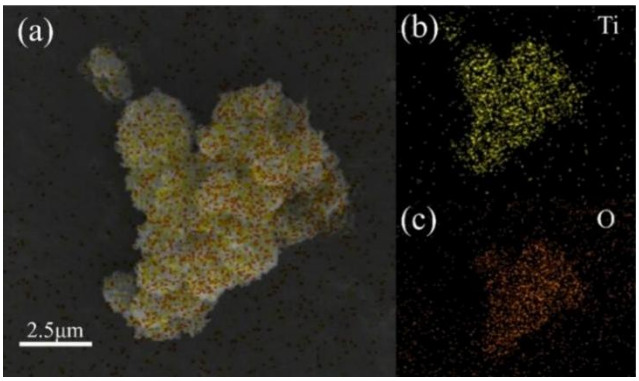

Figure 2. Elemental distribution maps of the as-prepared TiO_2 hollow spheres obtained by scanning electron microscopy (SEM): (a) overall elemental distribution, (b) Ti, (c) O

3.2. Evaluation of Photocatalytic Activity

The photocatalytic activity of the as-prepared nano-TiO_2 hollow spheres was evaluated by the degradation of Rhodamine B (RhB), a representative organic pollutant. In a typical experiment, 100 mg of nano-TiO_2 hollow spheres were accurately weighed and dispersed into 100 mL of RhB solution. The suspension was stirred in the dark for 20 minutes to establish adsorption-desorption equilibrium. Subsequently, a halogen lamp was turned on to initiate the photocatalytic reaction. At regular intervals of 10 minutes, 6 mL aliquots of the reaction mixture were withdrawn. The catalyst particles were removed by centrifugation, and the supernatant was analyzed using a UV-Vis spectrophotometer at the maximum absorption wavelength of RhB (554 nm). Figure 3 presents the UV-Vis absorption spectra of RhB solution during photocatalytic degradation by the nano-TiO_2 hollow spheres. During the 20-minute dark reaction period, the concentration of RhB decreased, and the adsorption capacity reached 5.4×10^{-6} mol/g, indicating that the prepared nano-TiO_2 hollow spheres possess strong physical adsorption properties. Their large specific surface area provides favorable conditions for physical adsorption. Upon initiation of the photocatalytic reaction, the absorption peak of RhB at 554 nm decreased rapidly. Meanwhile, a gradual blue shift of the absorption peak was observed, suggesting that RhB was decomposed into secondary organic intermediates. The absorption peak eventually flattened, indicating the completion of the degradation process.

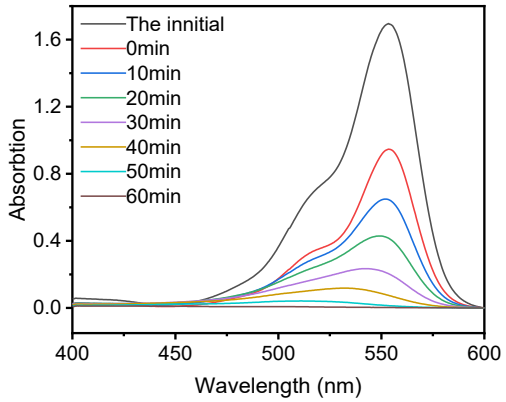

Figure 3. UV-Vis absorption spectra of RhB degradation over nano-TiO_2 hollow spheres at different time intervals

Comparing the as-prepared nano-TiO_2 with commercial P25 represents a widely recognized benchmark evaluation approach in photocatalysis research. P25, issued as a nanoscale standard reference material by the National Institute of Standards and Technology (NIST) of the United States, exhibits outstanding and stable photocatalytic activity under ultraviolet light owing to its unique mixed-phase structure comprising approximately 80% anatase and 20% rutile. It has long been regarded as the "gold standard" in the field. By conducting a parallel comparison with P25, the performance advantages and disadvantages of the synthesized nano-TiO_2-in terms of light absorption capacity, charge carrier separation efficiency, and pollutant degradation rate—can be objectively quantified. This allows for an accurate assessment of the actual effects of strategies such as morphology control, doping modification, or heterojunction construction. Furthermore, the intrinsic structure–activity relationship between material structural characteristics and catalytic performance can be elucidated. In addition, such a comparison can determine the competitiveness of the newly developed material relative to existing commercial products in practical application scenarios, including wastewater treatment and air purification, thereby providing a scientific basis for the exploration of subsequent optimization directions and potential application development.

Figure 4(a) presents the relationship between C_t/C_0 and irradiation time for the photocatalytic degradation of RhB using the as-prepared nano-TiO_2 hollow spheres and commercial P25. Figure 4(b) shows the corresponding plot of ln (C_t/C_0) versus time for both photocatalysts. The photocatalytic activity of the TiO_2 hollow spheres is significantly superior to that of P25. Under identical illumination conditions, after 60 minutes of reaction, the degradation efficiency of RhB by the TiO_2 hollow spheres reached 44%, whereas that of P25 was only 23%, representing an increase of 21 percentage points. Quasi-first-order kinetic fitting reveals that the reaction rate constant (k) of the TiO_2 hollow spheres is 1.0×10^{-2} min^{-1}, which is approximately 2.01 times that of P25 ($k = 4.97 \times 10^{-3}$ min^{-1}).

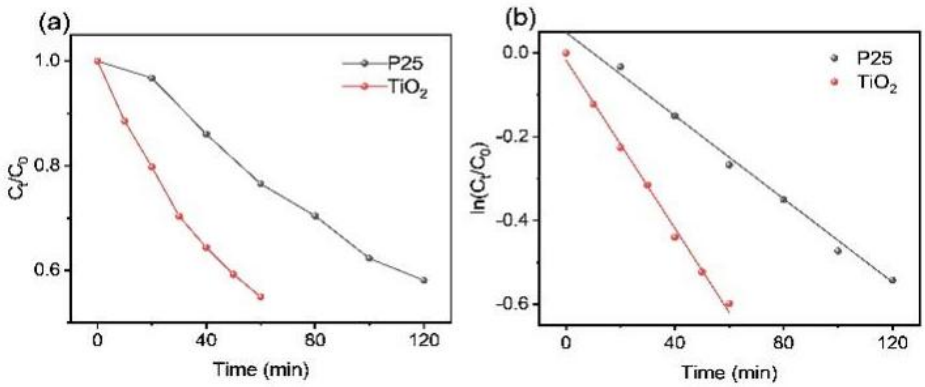

Figure 4. (a) C_t/C_0 vs. time for RhB degradation over TiO_2 hollow spheres and P25; (b) $\ln(C_t/C_0)$ vs. time for RhB degradation over TiO_2 hollow spheres and P25

4. Conclusion

This study addresses the key scientific challenges associated with the application of titanium dioxide (TiO_2) in photocatalysis, namely its narrow light response range, facile recombination of photogenerated charge carriers, and the tendency of nanoparticles to aggregate and resist recovery. To overcome these issues, a hollow spherical structure modification strategy was proposed to optimize the microstructure and physicochemical properties of TiO_2. The main conclusions of this study are summarized as follows:

Using a facile liquid-phase method with nano-TiO_2 microspheres as the precursor, the synergistic effect of PVP and NaF was employed under hydrothermal conditions to etch and optimize the microspheres, leading to the successful fabrication of TiO_2 micro-nanospheres with a hollow architecture. Scanning electron microscopy (SEM) characterization revealed that the as-prepared TiO_2 hollow spheres possessed distinct interior cavities and rough, porous shell surfaces.

Under halogen lamp irradiation, the photocatalytic degradation activity of the TiO_2 hollow spheres toward Rhodamine B (RhB) was significantly superior to that of commercial P25. Under optimal conditions (catalyst dosage: 30 mg/L; initial RhB concentration: 3×10^{-5} mol/L), the degradation efficiency of RhB by the TiO_2 hollow spheres was 21 percentage points higher than that of P25. Quasi-first-order kinetic fitting indicated that the reaction rate constant of the TiO_2 hollow spheres was approximately 2.01 times that of P25.

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