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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　　博士（工学）　　氏名　郭 龍飛

学 位 論 文 題 名

Design and Modification of Spinel Type Ferrites (MFe_2O_4, M = Zn & Ca) with Highly Efficient Photocatalytic Performance

(高効率光触媒性能を備えたスピネル型フェライト (MFe_2O_4, M = Zn & Ca) の設計と改良)

Organic pollutant in wastewater has become a severe environmental and safety problem. The semiconductor-based photocatalytic degradation is emerging as a high-efficiency and environmentally friendly approach because it only uses photocatalyst and solar energy. For the better utilization of visible light accounting for about 47.7% of solar energy, spinel type ferrites ($ZnFe_2O_4$ and $CaFe_2O_4$) with narrow bandgap (approximately 1.9 eV) are becoming emerging efficient photocatalysts. However, the serious photogenerated charges recombination limits the photocatalytic performance. To solve this problem, some modifications including forming heterojunction, fuel ratio changing, and shape modification have been carried out in this thesis.

In chapter 1, an overview of photocatalysis including photocatalytic dye degradation, water splitting, and CO_2 reduction was introduced first. Then a review on spinel type ferrite photocatalysts including common structure, and synthesis method was summarized. In the end, various modification methods of photocatalysts for enhanced photocatalytic properties were introduced.

In chapter 2, $ZnFe_2O_4/SnO_2$ composites were fabricated via a facile solution combustion synthesis (SCS) method for methylene blue (MB) degradation. The crystallite and morphology characterizations revealed that ZFO/SnO_2 composites have relatively small crystallite and particle size compared to pure ZFO. The introduction of SnO_2 remarkably improved the photocatalytic performance of pure ZFO catalyst. Specifically, $ZFO - SnO_2$ (10%) exhibited the highest photocatalytic degradation rate constant of 0.01970 min^{-1} in the composites, approximately 3.08 and 2.64 times higher than that of single ZFO (0.00640 min^{-1}) and SnO_2 (0.00747 min^{-1}), respectively. The band alignment analysis showed that the improvement of photocatalytic activity was due to the improved charges separation efficiency in the ZFO/SnO_2 composite. $ZFO - SnO_2$ (10%) with H_2O_2 showed the highest photo-Fenton degradation rate constant of 0.05301 min^{-1} and could remove 95.2% of MB within 60 min under irradiation.

In chapter 3, $CaFe_2O_4$ (CFO) was fabricated by solution combustion synthesis (SCS) method using different fuels (urea and glucose) and fuel ratios (0.5, 1.0, and 1.5). CFO-Glucose shows a smaller crystallite size than CFO-Urea sample. CFO-1.0 presents the smallest crystallite size among various fuel ratios products. CFO-1.0 photocatalyst presents the best photocatalytic MB degradation with a kinetic constant of 0.00372 min^{-1} compared to CFO-Urea (0.00123 min^{-1}), CFO-0.5 (0.00176 min^{-1}), and CFO-2.0 (0.00249 min^{-1}). Based on the PL and XPS characterizations, the efficient photocatalytic performance of CFO-1.0 is attributed to the efficient charge separation and suitable photocatalyst surface state.

In chapter 4, $CaFe_2O_4$ nanorods (CFO NRs) and aggregated particles (CFO APs) were fabricated with and without the help of molten salt-assisted shape modification, respectively. CFO APs present inferior photocatalytic performance due to the plenty of grain boundaries which hinder photogenerated charges transfer and act as charge recombination sites. Molten salt-assisted modification can easily change the shape of CFO NRs and significantly suppresses the formation of grain boundaries, facilitating photogenerated charges separation and transfer for highly efficient photocatalytic degradation of methylene blue (MB). Surface state investigation indicates a decreased amount of unsuitable oxygen vacancies and defects in CFO NRs, which is beneficial in alleviating the recombination of photogenerated charges in CFO NRs. The CFO NRs show a ten-time increased kinetic constant of MB degradation from 0.0013 to 0.013 min^{-1} by virtue of the alleviative charge recombination.

In chapter 5, an overall conclusion of this dissertation was presented. Overall, this thesis performed a systematic research on the design and modification of spinel type ferrites with highly efficient photocatalytic performance. This work also shows forming semiconductor heterojunction structure with suitable band position is an efficient way to enhance the photocatalytic performance of photocatalysts. The fuel ratio of SCS has a great effect on the final product composition and photocatalytic performance. Meanwhile, molten salt-assisted shape modification of photocatalyst is also an efficient way to improve their photocatalytic properties.