Improved visible-light photocatalytic activity of TiO₂ co-doped with copper and iodine

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Abstract

Cu-I-co-doped TiO₂ photocatalysts active to visible light absorption were prepared by hydrothermal method and calcined at various temperatures (350 °C, 450 °C, and 550 °C). The co-doped powders at 350 °C displayed the highest experimental Brunauer–Emmett–Teller surface area and lowest photoluminescence intensity, which demonstrated that a decrease in electron–hole recombination process. The synthesis of co-doped TiO₂ was performed at this optimized temperature. In the co-doped sample, the Cu²⁺ doped TiO₂ lattice created a major “red-shift” in the absorption edge due to the presence of the 3d Cu states, whereas the amount of red-shift from the I⁻ doping in the TiO₂ lattice was minor. Interestingly, the presence of Cu²⁺ species also boosted the reduction of I⁻ ions to the lower multivalence state I⁻ in the TiO₂ lattice by trapping the photogenerated electrons, which resulted in effective separation of the photogenerated charges. The Cu-I-co-doped TiO₂ was able to degrade methyl orange dye under visible-light irradiation with improved photocatalytic activity compared with the single metal-doped TiO₂ and pure TiO₂ because of the strong visible light absorption and effective separation of photogenerated charges caused by the synergistic effects of Cu and I co-dopants.

Keywords: Codoped TiO₂; Photocatalytic degradation; Visible light absorption; Methyl orange

1. Introduction

TiO₂ has received considerable attention as an ideal photocatalytic material for the degradation of organic contaminants from wastewater or gas phase due to its high photoactivity, good photostability, cost effectiveness, and environmental friendliness [1,2]. Unfortunately, the poor capability of TiO₂ to absorb visible light as a main part of solar spectrum has limited its large-scale industrial applications [3]. For increased utilization of sunlight, various modifications have been made to the crystal structure of TiO₂-based materials, such as metal doping or non-metal element doping [4–9], coupling [10–14], and co-catalyst modification [15,16] for the enhanced absorption of sunlight. Among them, ion doping (either metal or nonmetal) is considered a simple and effective modification method that has been undertaken by several research groups to extend the light absorption from UV to the visible region [17–20]. In general, the dopant ions in the TiO₂ lattice introduce mid-gap energy states at the top of the valence band or at the bottom of the conduction band of TiO₂, which extend its absorption band edge from the UV to the visible-light region [21–25]. These as-produced impurity energy levels can also function as a trapping center for the effective separation of photogenerated electron–hole pairs, thus leading to increased photocatalytic activity [26]. However, these dopant ions must be utilized in small quantities to prevent subsequent recombination of electrons and holes. However, low concentration doping causes only a slight red shift of the optical absorption edge to the visible-light region, which is insufficient for the effective utilization of visible solar light [1,27]. Considering the increased doping concentration, the impurity levels act as electron–hole pair recombination sites that cause a negative effect on the photocatalytic activity [28,29]. In other words, extending the absorption edge to the visible region at the same time to prevent electron–hole recombination is a challenging task.

Recently, co-doping with two different types of ions has become a highly useful approach to improve the visible light-driven photocatalytic activity of TiO₂. In such system, the synergic combination of different types of dopants not only enhances the absorption of visible light but also decreases the photogenerated charge carrier recombination [1,3,30]. The N and C nonmetal dopants in TiO₂ have been widely utilized as co-dopants with various metals,