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Hydrothermal synthesis and photocatalytic performance of metal-ions doped TiO_2

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ABSTRACT

Metal-ions doped TiO_2 (M-TiO_2) were synthesized using a hydrothermal method with a post-annealing process, including individual Ag^+, Cu^{2+}, Mn^{2+}, Ce^{3+}, Fe^{3+} and Zr^{4+} ions. Physical properties of the synthesized M-TiO_2 were characterized including XRD pattern, BET surface area, diffuse reflectance spectra and visible-light photoactivity tests. Total photocatalytic performances of M-TiO_2 were evaluated by degrading rhodamine b under whole solar-light irradiation with manganese-ions doped TiO_2 (Mn-TiO_2) showing the highest degradation efficiency. Compared to crystalline structure and visible-light photoactivity, BET surface area of M-TiO_2 particles exhibits the most significant impacts, showing a positive correlation with the total photocatalytic performance of M-TiO_2. Total photocatalytic efficiencies of Mn-TiO_2 were further optimized through synthesis with 3% of Mn doping concentration, 180 °C of hydrothermal treatment and 450 °C of post-annealing temperature.

1. Introduction

Titania (TiO_2) has been extensively studied as a photocatalyst for the degradation of environmental pollutants during the last decades because of its superior photocatalytic performance, non-toxicity, low production cost and high persistence to photocorrosion [1,2]. However, due to the large band gap energy (3.0–3.2 eV) of anatase TiO_2, most of commercially available TiO_2 catalysts are active only under UV-light spectral range, which is a small fraction (2–3%) of whole solar-light spectrum [3,4].

TiO_2 doped with metal ions [5–7] can effectively extend the absorption spectrum into visible-light range so as to take advantage of a wider range of solar spectrum to improve the photocatalytic performance under whole solar-light irradiation. Numerous metal-ions have been investigated as potential dopants, including iron [8], chromium [9], nickel [10], aluminum [11], silver [12], vanadium [13], cobalt [14], etc. It was hypothesized that the introduction of metal-ions into TiO_2 could improve the electronic energy band structure of TiO_2 and thus enhance the photocatalytic performance by effective charge transfer from the doping metal-ions to Ti^{4+}. For example, Choi et al. [15] reported that Pt and Cr ions doped TiO_2 catalysts showed significantly enhanced photocatalytic performance under visible-light compared with pure TiO_2 for all three photodegradation of methylene blue, oxidation of iodide, and oxidative degradation of phenol.

There is a considerable controversy on the effect of doping metal-ions on photocatalytic performance. Some papers reported that the doping of metal-ions such as W^{6+}, V^{5+}, Fe^{3+} and Cu^{2+} in TiO_2 increased the resultant photocatalytic performance [16,17] whereas Nagaveni et al. demonstrated that TiO_2 doping with these metal-ions through solution combustion method showed weaker photocatalytic performance than pure TiO_2 [18]. Such wide variations in reported literatures should be mainly due to different preparation methods and doping elements which resulted in different physical properties of TiO_2 particles although similar in their visible-light photoactivity. For example, conventional sol–gel synthesis of metal-ions doped TiO_2 (M-TiO_2) often suffers from poor dispersion of the doped element in ethanol-containing solution, resulting in crystalline phase segregation of doping metal oxides from TiO_2 lattice, and weaker photocatalytic performance of TiO_2 [19]. While ion impregnation method is commonly employed to prepare M-TiO_2, substitution of metal-ions occurs only on the surface of TiO_2 particles or films, rather than in the bulk TiO_2 crystals, causing weak photocatalytic performance [20]. Generally, TiO_2 particles with smaller size and higher surface area exhibit higher photocatalytic performance due to quantum confinement effects [21]; anatase TiO_2 with a small amount of rutile is also significant for high photocatalytic performance. A typical example is the commercially available Degussa P25 TiO_2 with 80% anatase and 20% rutile [22,23], showing higher photocatalytic performance than its pure counterpart. Hence, it is critical to select appropriate methods and suitable doping elements to synthesize M-TiO_2 catalysts with desired properties to enhance photocatalytic performance under solar-light irradiation.

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