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The effect of fabrication method of hierarchical 3D TiO_2 nanorod spheres on photocatalytic pollutants degradation

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ABSTRACT

The effect of fabrication method on the properties of hierarchical 3D TiO_2 nanostructures was investigated by employing and developing both hydrothermal method and calcination method to synthesize hierarchical 3D TiO_2 nanorod spheres in this study. A comprehensive comparison in terms of morphologies, crystallization, specific surface areas, light absorption capabilities, and photoluminescence spectrum was conducted between 3D TiO_2 nanorod spheres synthesized via hydrothermal method and that synthesized via calcination method. A better photocatalytic activity was demonstrated over the TiO_2 nanorod spheres synthesized through calcination method. This was ascribed to the better crystallization and monodispersion of the hierarchical 3D TiO_2 nanorod spheres resulted from the calcination method; thus rendering it with more superior characteristics such as larger specific surface area, enhanced light absorption capability and faster transfer of electrons which suppress the recombination of photogenerated electrons and holes. This study is thus significant not only in promoting the development of hierarchical 3D TiO_2 nanorod spheres via different methods, but also in revealing the effect of fabrication method on the photocatalytic activity of hierarchical 3D TiO_2 nanorod spheres. The calcination method is proposed to be a facile and promising method for scale-up production of the hierarchical 3D TiO_2 nanorod spheres with high photocatalytic activity for efficient pollutants degradation.

1. Introduction

Owing to its unique properties such as environmental benign, low cost, chemical stability and high photocatalytic activity, TiO_2 has attracted considerable attentions and have been widely employed in a broad field of applications in the past decades [1–5]. In tandem with the rapid development of nanotechnology [6], dimensionality and size of nanomaterials have been paid much attentions owing to their significances in dominating the photocatalytic performances of TiO_2 [7,8]. Three-dimensional (3D) TiO_2 nanostructures made up of one dimensional (1D) TiO_2 such as nanorods has been widely developed and used in photocatalysis [9,10], dye-sensitized solar cell (DSSC) [11,12], and electrochemistry [13] because of its unique porous microstructure which renders large specific surface area and therefore the fast transfer of electrons [14,15]. Meanwhile, 3D TiO_2 nanostructures consisted of 1D nanorods (TiO_2 nanorod spheres) is one kind of typical hierarchical structured nanomaterial with multi-scaled organizations [10]. Similar to the hierarchical structure of natural forest with high photosynthetic efficiency [10,16–19], hierarchical 3D TiO_2 nanorod spheres also offer a lot of merits which are beneficial for the improvement of photocatalytic activity, such as (1) the enhanced light absorption capability by permitting more lights reflection and multiple-scattering inside its interior, (2) enlarged specific surface areas thus providing more reaction sites for enhanced mass transfer, and (3) enhanced charge transfer facilitated by 1D TiO_2 nanorod structure thus retarding the recombination of photogenerated electrons and holes [10,16,20].

Wet-chemistry based hydrothermal method is popularly used for the synthesis of TiO_2 nanorod spheres. TiO_2 nanorod hemispheres were successfully grown on glass slide with a well tuned hydrothermal method and displayed super switchable hydrophilic/hydrophobic surface properties [21–23]. However, in this synthetic process, there are some key factors which play significant roles in influencing the morphology and the growing direction of 1D TiO_2 nanorods. First of all, the glass slide is necessary to assist the nucleation of TiO_2 and influence the radial growth of the subsequently formed TiO_2. Secondly, the acidic condition and the Cl^- in the reaction solution dominate the crystal phase of TiO_2 and the growing direction of 1D TiO_2, respectively [24,25]. Strong acidic condition favors the formation of rutile TiO_2, while the Cl^- adsorbed on the (1 1 0) plane of rutile TiO_2 could suppress and accelerate the growth of TiO_2 in the [1 1 0] and [0 0 1] direction, respectively, following which long 1D TiO_2 nanorods could be formed [25]. Some researchers have also reported the synthesis of 3D TiO_2 nanostructures made up of long 1D nanoribbon/wires through hydrothermal

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