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Hollow TiO_2 spheres with improved visible light photocatalytic activity synergistically enhanced by multi-stimulative: Morphology advantage, carbonate-doping and the induced Ti^{3+}

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ABSTRACT

Great efforts have been devoted to improve the photocatalytic activity of TiO_2 in the visible light region. Rational design of the external structure and adjustment of intrinsic electronic status by impurity doping are two main effective ways to achieve this purpose. A facile one-pot synthetic approach was developed to prepare C-doped hollow TiO_2 spheres, which simultaneously realized these advantages. The synthesized TiO_2 exhibits a mesoporous hollow spherical structure composed of fine nanocrystals, leading to high specific surface area (~180 m^2/g) and versatile porous texture. Carbonate-doping was achieved by a post-thermal treatment at a relatively low temperature (200°C), which makes the absorption edge red-shifted to the visible region of the solar spectrum. Concomitantly, Ti^{3+} induced by C-doping also functions in improving the visible-light photocatalytic activity by reducing the band gap. There exists a synergistic effect from multiple stimulatives to enhance the photocatalytic effect of the prepared TiO_2 catalyst. It is not out of expectation that the as-prepared C-doped hollow TiO_2 spheres exhibits an improved photocatalytic activity under visible light irradiation in organic pollutant degradation.

Introduction

Titanium dioxide (TiO_2), a well-known and important environmental and energy material, has been intensively studied because of its wide band gap, environmental friendliness, low cost and the large spectrum of application fields (Chen and Mao, 2007; Ge et al., 2016; Hassan et al., 2016; Nakata and Fujishima, 2012; Song and Paik, 2016). It has been proven that the properties and application efficiency of TiO_2 depend considerably on its crystallinity, morphology, texture, size and dimensionality (Li and Liu, 2011; Liu et al., 2013; Wang et al., 2014). When TiO_2 was used as a photocatalyst, it intentionally strengthens several properties that can effectively improve its application efficiency, which includes the following: (1) high specific surface area for high photocatalytic activity and adsorption capacity; (2) hierarchical texture structure for efficient light-harvesting through multi-reflection of the incoming light; (3) large enough particle size for convenient separation; and (4) rational doping for extension of light absorption edge to visible light region. Whereas these facilitation measurements

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have usually been met individually, which result in limited improvement of application efficiency, simultaneously achieving all of them to synergistically improve the photocatalytic activity has rarely been reported, and therefore remains a great challenge.

In view of the first two abovementioned techniques for improving catalytic activity (high specific surface area and the hierarchical structure), TiO_2 with hollow structures has been proven an effective approach (Joo et al., 2013; Li et al., 2013; Li and Shi, 2014). On the one hand, constructions of hierarchical hollow structure usually possess higher specific surface area for their overall hollow structure and the sublevel porous texture of the subunits building blocks. On the other hand, constructing hollow structure is a potent technique to realize higher light-harvesting efficiency through multi-reflection/diffraction of the incoming light not only in the hollow voids but also in the pore channels (Li et al., 2013, 2016). Specifically, hollow structure materials have attracted considerable attention as an important family of functional materials recently because of their unique characteristics such as low density, high surface-to-volume ratio, and low coefficients of thermal expansion and refractive index compared to their solid counterparts, which in turn endows them with many promising applications in a wide range of fields, *e.g.*, photocatalysis, energy storage and conversion, drug delivery, nanoreactor, and many others (Chen et al., 2013; Hu et al., 2011; Lou et al., 2008; Si et al., 2016). Various strategies have been developed to controllably synthesize hollow structures of different materials (Joo et al., 2013; Zhang et al., 2009). Owing to the advantage of narrow size distribution products with well-defined structural features, template approaches are the most frequently adopted strategies. Fu's group reported a typical template method for synthesis of hollow TiO_2 spheres (Shi et al., 2012, 2012). They used carbon spheres as a hard template on which Ti species were deposited. Hollow TiO_2 spheres were obtained upon removal of the carbon template. However, there are inherent drawbacks: (a) pre-fabrication of template material/conditions or pre-functionalization of the template surface, (b) tedious procedures for shell deposition and template removal, and (c) incidents of shell collapse happened during template removal process. Another emerging strategy for synthesizing hollow structures is the template-free approach involving Kirkendall effect, Ostwald ripening, self-template, and chemically induced self-transformation (Chen et al., 2009; Ma et al., 2015; Su et al., 2017; Wang et al., 2013). However, the morphological uniformity and interior complexity of the hollow products by these strategies are generally less controllable. Thus, simple one-pot method for rationally synthesizing hollow structures without using any template would be appreciated in order to avoid the abovementioned drawbacks. Therefore, it is highly desirable to develop facile, scalable template-free approaches for the rational synthesis of hollow structures.

TiO_2 is a wide band semiconductor, which confines its light absorption only in the ultraviolet region of the solar spectrum, and thus makes it suffer from relatively fast electron–hole recombination (nsec-μsec domain). Impurity-doping has, so far, been proven to bestowing the ability of enhance the absorption in the visible region of the solar spectrum by either introducing sub-bandgap states or reducing the bandgap width (Chen and Mao, 2007; Dahl et al., 2014). Among numerous metals (Au, Ag, Fe, Zn, Co, *etc.*) (Ali et al., 2012; Chen et al., 2014; Chowdhury et al., 2017; Feng et al., 2013; Ola and Maroto-Valer, 2016; Shuang et al., 2016; Wang et al., 2013) and nonmetal ions (C, B, F, S, N, *etc.*) (Asahi et al., 2001; Lin et al., 2013; Liu et al., 2014; Xu et al., 2010; Yu et al., 2002) doping, C-doping has been proven to be an outstanding one on extending the light absorption edge of TiO_2 from ultraviolet (UV) to visible light region for the following reasons: (1) carbon has a large electron-storage capacity and can accept the photon-excited electrons to enhance the separation of photo-generated carries (Kongkanand and Kamat, 2007; Zhang et al., 2013); (2) carbon endows the catalyst with a wide range of visible light absorption at wavelength of 400–800 nm, which facilitates charge transfer from the bulk to the surface region where the desired oxidation reaction takes place (Lee et al., 2013). The developed doping methods to date include sol–gel method with carbon precursors, annealing TiO_2 under CO gas flow at high temperature, high temperature sintering of a carbon-containing TiO_2 precursor (Dong et al., 2011; Lee et al., 2013; Li et al., 2012; Park et al., 2009). However, these methods have their limitations. Usually, additional external carbon precursors and high temperature treatment (400–850°C) are required; undesirable gaseous byproducts are produced; the texture structure of the TiO_2 is easily damaged under high temperature treatment; by the way, the synthetic procedures are somewhat tedious. Thus, developing efficient approaches featuring low temperature, free of using excessive toxic reagents and producing harmful byproducts, and facile preparation procedures remains a great challenge.

Inspired by the abovementioned considerations, we present here a facile one-pot, cost-effective method for preparation of the C-doped hollow TiO_2 spheres (CDHTSs) with tunable architecture, high crystallinity, high specific surface area, and high visible light absorption ability, which can simultaneously realize rational design of the external structure and the adjustment of intrinsic electronic status. Compared to traditional strategies, it is free of sacrificial templates and complicated preparation procedures. The obtained mesoporous hollow structure successfully endows the TiO_2 catalyst with high specific surface area, as well as high light harvesting efficiency. By the way, C doping could be simultaneously realized through a low-temperature annealing process without damaging the texture and structure of the TiO_2 hollow spheres, enabling the as-prepared TiO_2 with high catalytic activity in the visible light region. As a result, the as-prepared C doped TiO_2 with hierarchical hollow structure simultaneously met the abovementioned four facilitation measurements, *e.g.*, high specific surface area, hierarchical texture structure, large particle size and effective C doping, which can maximally enhance the visible light photocatalytic activity of the product as expected.

1. Experimental

1.1. Materials

Titanium butoxide (TBOT), titanium isopropoxide, ethanol (>99%), and acetone were used as purchased from Sigma-Aldrich. Ultrapure deionized water (>17 MΩ/cm) used throughout the experiments was obtained from a Millipore Milli-Q system.

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