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Invited article

Review of the progress in preparing nano TiO_2: An important environmental engineering material

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ABSTRACT

TiO_2 nanomaterial is promising with its high potential and outstanding performance in photocatalytic environmental applications, such as CO_2 conversion, water treatment, and air quality control. For many of these applications, the particle size, crystal structure and phase, porosity, and surface area influence the activity of TiO_2 dramatically. TiO_2 nanomaterials with special structures and morphologies, such as nanospheres, nanowires, nanotubes, nanorods, and nanoflowers are thus synthesized due to their desired characteristics. With an emphasis on the different morphologies of TiO_2 and the influence factors in the synthesis, this review summarizes fourteen TiO_2 preparation methods, such as the sol–gel method, solvothermal method, and reverse micelle method. The TiO_2 formation mechanisms, the advantages and disadvantages of the preparation methods, and the photocatalytic environmental application examples are proposed as well.

Contents

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Introduction

Tremendous environmental problems evolved with the fast development of civilization, such as the remediation of contaminated groundwater, the control of toxic air and the alleviation of global warming. In order to address these issues, extensive research is underway (Bhatkhande et al., 2002; Hardoy et al., 2013; Hoffmann et al., 1995). Since the discovery of photosensitization effect of TiO_2 electrode on water electrolysis into H_2 and O_2 by Fujishima and Honda in 1972 (Fujishima and Honda, 1972), photocatalysis has generated a large scope of attention. If these environmental problems can be solved with photocatalysis, lots of energy would be saved without secondary pollution. With more than forty years of development, TiO_2 has become the most popular photocatalyst to solve environmental problems and different methods have been applied to synthesize nanoscale TiO_2 (Chen and Mao, 2007; Lei et al., 2010; Shamaila et al., 2010; Ye and Lu, 2013; Zhang and Liu, 2008). Up to now, TiO_2 has been applied in various photocatalytic environmental applications such as water purification, CO_2 conversion, and air pollution control with promising results (Danaei Kenarsari et al., 2013; In et al., 2012; Ma et al., 2013; Natoli et al., 2012; Z.Y. Sun et al., 2011; Tang et al., 2010; G.M. Wang et al., 2011; D.Q. Zhang et al., 2010). Moreover, the TiO_2 applied, eco-friendly, photocatalytic, commercial products, for instance, self-cleaning glass and surface sterilization tools, have also been demonstrated to be effective and of great value (Fujishima et al., 1999).

TiO_2 is an n-type wide bandgap semiconductor and has three crystalline phases in nature, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Rutile TiO_2 is the most stable form, whereas anatase and brookite phases are metastable and can be transformed to rutile phase when heated under high temperature (~750°C) (Liao et al., 2012). Anatase and rutile TiO_2 are most often reported as photocatalysts, and some research results recently demonstrated that a mixed form of rutile and anatase TiO_2 displayed enhanced photocatalytic ability, since the transfer of electrons from anatase to a lower-energy rutile electron-trapping site in a mixed-phase could reduce the recombination rate of charge carriers in anatase TiO_2 and effectively create catalytic “hot spots” (Buonsanti et al., 2008; Kho et al., 2010; G.H. Li et al., 2008). The report of the photocatalytic performance of brookite TiO_2 started only a few years ago due to the hard preparation of pure brookite TiO_2 and its relatively poor photoreactivity (Kandiel et al., 2010; Lin et al., 2012; B. Zhao et al., 2009).

Despite which type of TiO_2 it is, bulk TiO_2 has little photocatalytic ability. The good properties of nano TiO_2 are owing to its low dimensionality and quantum size effect. TiO_2 nanocrystals have several advantages over their bulk counterparts in terms of potential applications because of their high surface-to-volume ratio, increased number of delocalized carriers on the surface, improved charge transport and lifetime afforded by their dimensional anisotropy, and the efficient contribution in the separation of photo-generated holes and electrons (Anpo and Takeuchi, 2003; Bavykin et al., 2006; Evtushenko et al., 2011). Because of this, it is essential to control the particle size, shape, and distribution of the prepared TiO_2. A variety of TiO_2 nanostructures have thus been prepared, such as nanoparticles, nanotubes, nanorods, nanofibers, and nanoflowers, due to their desired characteristics, and these structures can be made through various preparation methods, including the sol–gel method, hydrothermal method, microwave method, and reverse micelle method. (Chen et al., 2010; Dai et al., 2011; Dutta et al., 2012; Haouemi et al., 2011; Kwon et al., 2008; Luo et al., 2009; Mali et al., 2012; Yang et al., 2011). In reviewing the synthesis of TiO_2 nanomaterials, a typical procedure and representative scanning or transmission electron microscopy images are presented to give a direct impression of how these nanomaterials are obtained and how they normally appear. The influence of different reaction conditions on the morphology and structure is stated and the mechanism of nucleation and growth, as well as processes such as aggregation and coarsening, is given. A table is listed after most of the preparation methods containing various TiO_2 materials prepared by that specific method, typical physicochemical properties and tested photocatalytic environmental applications. Comments are also made on these preparation methods about their advantages and disadvantages. For detailed instructions on each synthesis, the readers are referred to the corresponding literature.

As it is known, many reviews about TiO_2 have been reported and the comprehensive review by Chen and Mao (2007), which covered hundreds of studies until the period before 2006, stands out as a great reference. Whereas significant progresses have been made in the last few years on the preparation of TiO_2, a new and thorough review containing the new and representative approaches to the synthesis and investigation of TiO_2 is needed to analyze the latest advances in the preparation of TiO_2 for obtaining nanomaterials based on it.

1. TiO_2 preparation methods

1.1. Sol–gel method

The sol–gel method has generated a large scope of interest in the preparation of inorganic ceramic and glass materials. This simple, cost effective and low temperature synthesis procedure has also been favored and largely applied in catalyst preparation due to its potential to fabricate catalysts with high purity, homogeneity, fine-scale and controllable morphology. Various photocatalysts have been fabricated by the sol–gel process, including ZrO_2, $SrTiO_3$, ZnO, WO_3, and TiO_2. (Chen et al., 2011; Djaoued et al., 2013; Y.M. Sun et al., 2011; Yu et al., 2011). The sol–gel procedure includes the process of hydrolysis and polycondensation, during which process M–OH–M or M–O–M bridges are established between the metallic atoms M of the precursor molecules, resulting in oxides or hydroxides at last. Specifically for TiO_2, titanium alkoxides (such as titanium isopropoxide, titanium n-butoxide), alcohol, and acid/water are introduced into the reaction system. After stirring for several hours, densely cross-linked three-dimensional structures are built and terminated as TiO_2 gel. The reaction mechanism is as follows (Gupta and Tripathi, 2012; W. Li et al., 2012; Macwan et al., 2011): the hydrolysis reactions:

$$Ti(OR)_n + H_2O \rightarrow Ti(OH)(OR)_{n-1} + ROH \quad (1)$$