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Critical review

One-dimensional titania nanostructures: Synthesis and applications in dye-sensitized solar cells

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ABSTRACT

One-dimensional (1D) titania (TiO_2) in the form of nanorods, nanowires, nanobelts and nanotubes have attracted much attention due to their unique physical, chemical and optical properties enabling extraordinary performance in biomedicine, sensors, energy storage, solar cells and photocatalysis. In this review, we mainly focus on synthetic methods for 1D TiO_2 nanostructures and the applications of 1D TiO_2 nanostructures in dye-sensitized solar cells (DSCs). Traditional nanoparticle-based DSCs have numerous grain boundaries and surface defects, which increase the charge recombination from photoanode to electrolyte. 1D TiO_2 nanostructures can provide direct and rapid electron transport to the electron collecting electrode, indicating a promising choice for DSCs. We divide the applications of 1D TiO_2 nanostructures in DSCs into four parts, that is, 1D TiO_2 nanostructures only, 1D TiO_2 nanostructure/nanoparticle composites, branched 1D TiO_2 nanostructures, and 1D TiO_2 nanostructures combined with other materials. This work will provide guidance for preparing 1D TiO_2 nanostructures, and using them as photoanodes in efficient DSCs.

Contents

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1. Introduction

Since Iijima discovered fullerene-related carbon nanotubes in 1991, one-dimensional (1D) nanomaterials have attracted considerable attention because of their unique physical and chemical properties compared to their bulk counterparts [1]. These attractive properties can be tailored via changing their nanoscaled 1D morphologies. In recent years, 1D semiconducting oxide nanomaterials (ZnO, Nb_2O_5, In_2O_3, SnO_2, etc.) with different morphologies, such as nanorods [2,3], nanowires [4,5], nanotubes [6,7], nanofibers [8,9] and nanobelts [10,11], have been attracting great research interest due to their unique properties and potential applications. As one of the most important semiconducting oxide materials, titania (TiO_2) has a wide range of applications including paints, cosmetics, biomedicine [12–14], sensors [15,16], energy storage [17,18], solar cells [19–22], and photocatalysis [23–26] owing to its advantageous characteristics such as non-toxicity, high chemical stability, low-cost, high photocatalytic activity, and strong optical absorption. 1D TiO_2 nanostructures with controllable physical and surface properties have shown outstanding performance and versatility in a wide range of applications [27–32]. In the past decade, various synthetic methods were developed for the fabrication of 1D TiO_2 nanostructures. To highlight the research progress in 1D TiO_2 nanostructures and promote better use of 1D TiO_2 nanomaterials in the future, it is necessary to summarize these synthetic methods.

Undoubtedly, energy is one of the biggest challenges ahead for humankind in the 21st century. The world energy demand has reached 15 TW in 2010, according to a survey of the U.S. energy information administration (EIA) [33], and is predicted to reach 28 TW by 2050 and 46 TW by 2100 [34]. Continual increase in energy consumption has greatly accelerated the depletion of fossil fuels, subsequently triggering a series of problems, such as serious environmental pollution, the greenhouse effect and so on. Of the various renewable energy options, solar energy is regarded as an ideal solution to the energy and environmental challenge because of its abundance and cleanliness. A solar cell is an electronic device that converts solar energy directly into electricity by the photovoltaic effect. Among the different kinds of solar cells, dye-sensitized solar cells (DSCs), known as third generation solar cells, have become a hot topic over recent years [19,35–40]. In comparison with conventional silicon and compound semiconductor solar cells, DSCs exhibit some specific advantages including low manufacturing cost, facile fabrication processes and compatibility with flexible substrates. A historic breakthrough in DSCs was initially reported by O'Regan and Grätzel in 1991 [41]. Using a ruthenium dye as the sensitizer, a wide bandgap nanocrystalline semiconductor (TiO_2 nanoparticle) film, and an organic solvent-based electrolyte, a power conversion efficiency (PCE) as high as 7.1% was obtained under air mass (AM) 1.5 global sunlight. To date, PCE has been increased to 15% utilizing a perovskite material as a light harvester and an organic hole transport material to replace the traditional liquid electrolyte [42]. Although TiO_2-based DSCs have demonstrated the best cell efficiencies, many other semiconductor oxides such as ZnO and SnO_2 have also been employed as photoanode materials, showing good photo-electricity properties [43–49]. A schematic diagram of the interior of a DSC is shown in Fig. 1 [39]. During operation, optically excited dye molecules inject electrons into the conduction band of the semiconductor. The injected electrons diffuse through the nanocrystalline network to arrive at the back contact and then through the external load to the counter electrode. The original state of the dye molecules is subsequently restored by I^-, forming extra I_3^-. The I^- is recovered in turn by the reduction of I_3^- at the counter electrode. This completes a circuit.

In a DSC system, a high surface area mesoscopic photoanode is necessary to ensure sufficient dye loading, contributing to efficient light harvesting and an improvement in conversion efficiency. TiO_2 nanoparticles are the most used photoanode materials, which is due to the high surface area and the ease of fabrications. However, TiO_2 nanoparticles have numerous grain boundaries and surface defects. Besides, electron transport in nanoparticle-based DSCs has been proposed to occur either by a series of hopping events between trap states on neighboring particles or by diffusive transport within extended states slowed down by trapping/detrapping events [50,51]. Further improvement of PCE for those nanoparticle-based DSCs becomes more and more difficult due to these defects and limited electron transport.

1D TiO_2 nanostructures having high crystallinity and few grain boundaries and trap defects can provide rapid electron transport in photoanodes. A rapid electron transport may lower the opportunity of photogenerated electrons to contact with the positive species in the electrolyte, resulting in reduced charge recombination and potential benefits in achieving high performance DSCs [52]. Zhu et al. found that the charge recombination in TiO_2 nanotube film was 10 times slower than that in a TiO_2 nanoparticle film [53]. Up to now, many situations for applying 1D TiO_2 nanostructures in DSCs have been developed. The photoanodes made of 1D TiO_2 nanostructures alone provide direct pathways for electron transport [54–56] which, however, also have some disadvantages such as insufficient surface area and inefficient attachment of dye molecules. To overcome these drawbacks, 1D TiO_2 nanostructure/nanoparticle composites [57] and branched 1D TiO_2 nanostructures [58,59] have been developed to increase the surface area and retain effective electron transport. In addition, 1D TiO_2 nanostructures can be doped to decrease charge recombination and improve charge transfer [60,61].

To this end, we review herein the synthetic methods for 1D TiO_2 nanostructures and corresponding and promising applications in using 1D TiO_2 nanostructures as photoanode materials for efficient DSCs. In the first section, a comprehensive summary of the fabrication of 1D TiO_2 nanostructures is presented, and then applications of 1D TiO_2 nanostructures in DSCs are reviewed, focusing on 1D TiO_2 nanostructures only, 1D TiO_2 nanostructure/nanoparticle composites, branched 1D TiO_2 nanostructures, and 1D TiO_2 nanostructures combined with

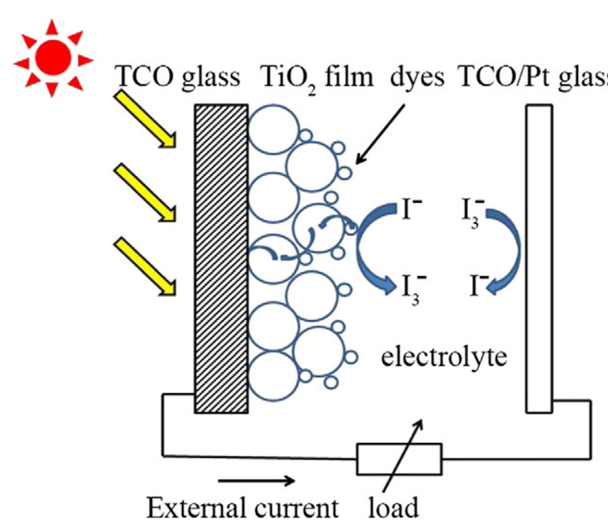

Fig. 1. Schematic diagram of a DSC.
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