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Microwave-assisted synthesis of titanium dioxide nanocrystalline for efficient dye-sensitized and perovskite solar cells

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Abstract

A rapid microwave-assisted hydrothermal synthetic method is reported for the fabrication of TiO_2 nanoparticles. Their photovoltaic activities are performed in dye-sensitized and perovskite-based solar cells. Power conversion efficiencies using microwave-assisted synthesized TiO_2 are relatively similar compared with those employed TiO_2 nanoparticles made of conventional hydrothermal process. The reaction time that is typically 12 h (literature value) was greatly reduced to only 25 min using microwave-heating process for TiO_2 nanoparticles formation, which provides an energy-saving and cost-effective method for making the building blocks of photoactive TiO_2 nanocrystallines. The material properties of the microwave-synthesized TiO_2 nanoparticles are characterized in details by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, fourier transform infrared spectroscopy and photoluminescence emission spectra. An optimal dye-sensitized solar cell with impressive power conversion efficiency of 8.2% was achieved using microwave-synthesized nanoparticles in combination with commercial paste (CCIC HPW-400) as scattering layer. A mesoscopic perovskite-based solar cell employing microwave-assisted synthesized TiO_2 nanoparticles obtained power conversion efficiency over 10%.

Keywords: Titanium dioxide; Dye-sensitized solar cells; Microwave-assisted synthesis; Perovskite solar cells

1. Introduction

After nearly two decades' research and development, dye-sensitized solar cells (DSCs) have been greatly attracting academic and commercial interest as promising inexpensive alternatives to conventional semiconductor-based photovoltaic devices (Grätzel, 2001; O'Regan and Grätzel, 1991). As a new and emerging renewable energy technology, the best conversion efficiency of 12% has been reported (Yella et al., 2011; Yum et al., 2014). Dye-sensitized solar cells contain three main device components: an electron-conducting mesoporous network of wide band-gap oxide semiconductor on which light-absorbing dyes are adsorbed, electrolyte composed of hole conducting medium and platinized catalytic counter electrode. The mesoporous network serves as an electron collector and

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an extremely high surface area scaffold hosting light harvester. Nanocrystalline TiO_2, a material that is abundant and chemically stable, is widely used for working electrode in photovoltaic devices, photocatalyst coatings, photoelectrochemical system, lithium (or sodium) batteries, chromatic display and so on (Byrne et al., 2014; Fujishima and Honda, 1972; Laskova et al., 2014; Periyat et al., 2010; Wu et al., 2014). For most of the highly efficient DSCs devices, their IPCE responses are nearly 90% at the dye-absorbing region, which implies the charge collection efficiency is close to unity (Grätzel, 2009; Yella et al., 2011). So far, these best-performing devices employed nanocrystalline TiO_2 made of hydrothermal autoclaving procedure (Ito et al., 2008; Wang et al., 2003). However, the conventional hydrothermal method for the fabrication of high quality nanocrystalline TiO_2 is time-consuming and requires elaborate processes (Ito et al., 2008). Several compromised solutions such as using commercial available powder as starting materials (Chang et al., 2013; Ito et al., 2007), or nonaqueous synthesis routes (Stefik et al., 2013) have been applied to DSCs electrodes for delivering high efficiency. Various nanostructure of nanotube (Jen et al., 2013; Tetreault and Gratzel, 2012), nanofiber (Sabba et al., 2014), nanorods (Yang et al., 2013), nano-composite (Wu et al., 2013a,b), or hierarchical architectures (Lan et al., 2013; Sauvage et al., 2010; Tetreault and Gratzel, 2012; Wu et al., 2013a,b) have been applied to fabricate photoanodes for the purpose of high efficiency device. However, elaborate process in controlling the nanoscale structure is not very straightforward for mass production. Therefore, in order to develop a low energy budget and convenient procedure for the preparation of nanocrystlline TiO_2, we propose a method to replace the step of autoclaving in conventional hydrothermal procedure by microwave heating with a focused microwave-assisted reactor (Model Discovery, CEM Corporation). The microwave-synthesized TiO_2 is analyzed thoroughly for the material properties and its photovoltaic characteristics.

Komarneni et al. first used microwave-assisted method to synthesize TiO_2 particles (Komarneni et al., 1999). Since then, to ameliorate the preparation of TiO_2 using microwave-assisted method, studies using microwave-assisted synthesis have been conducted for the preparation of TiO_2 crystal (Ding et al., 2007; Hart et al., 2004; Li et al., 2009; Periyat et al., 2010; Ribbens et al., 2008; Wilson et al., 2006; Wu and Tai, 2013; Zhang et al., 2009; Zumeta et al., 2009). The microwave-assisted method is an efficient alternative as it allows swift heating to the set temperature and extremely rapid crystallization, leading to the simplification of the preparation procedure (Baghbanzadeh et al., 2011; Baldassari et al., 2005; Bilecka and Niederberger, 2010; Niederberger, 2013). Another virtue of the microwave process is their easy adaptation to the conventional heating processes for the industrial usage. Moreover, its unique advantages of volumetric heating and energy saving in comparison with the conventional hydrothermal method are impressive (Baghbanzadeh et al., 2011). Recently the microwave synthesis has been applied to fabricate TiO_2 or titanate with great success for dye solar cells or battery (Chen et al., 2013; Huang et al., 2011; Manseki et al., 2013; Parmar et al., 2011; Shen et al., 2014; Wang et al., 2011). Lately, mesoscopic or thin film TiO_2 has shown its great importance for perovskite solar cells. PSCs using TiO_2 as mesoporous layer has achieved power conversion efficiency over 16% while the thin film perovskite solar cell using compact TiO_2 received 19% (Jeon et al., 2014; Zhou et al., 2014).

In this article, we emphasize on the microwave method that significantly reduced thermal history and energy budget for synthesizing TiO_2 nanocrystallites in comparison with the conventional hydrothermal process. Moreover, the microwave-synthesized material is capable of offering comparable photovoltaic performances, both for DSCs and PSCs, to the one prepared by conventional hydrothermal or commercial available materials. We have successfully used microwave-heating method to fabricate TiO_2 nanoparticles as building blocks for highly transparent mesoscopic thin film which is beneficial for optical penetration. Besides, compared with the reaction time required for crystallization in hydrothermal autoclaving, our focused microwave-assisted heating greatly reduced the process from 12 h to 25 min. As a result, DSCs using these crystals delivered a remarkable performance of power conversion efficiency of 8.2%, which ranks high among the reported microwave-synthesized TiO_2 for DSCs. Meanwhile, we also applied this microwave-synthesized nanoparticles to fabricate organometal halide perovskite solar cells, delivering device efficiency close to 11%. This result presents the first application of microwave-synthesized nanoparticles in organic–inorganic hybrid perovskite-based solar cells.

2. Experimental

The experimental procedure is illustrated in Scheme 1 with all the detail processes described in the following sections.

2.1. Materials

Commercially available titanium(IV) isopropoxide (TIP, 98%), ethanol (J.T.Baker, 99.5%), acetic acid (J.T.Baker, 100%), P25 TiO_2 powders (Degussa), nitric acid (Sigma–Aldrich, 65%) and PbI_2 (Sigma–Aldrich, 99.999%) were used as received. Two kinds of pure powders of ethyl celluloses (#46070, Fluka; #46080, Fluka) were dissolved in an ethanol solution with 5 wt% content of each ethyl cellulose (the total ethyl cellulose is 10 wt% in ethanol). The N719 dye powder (Solaronix) was used as received. Commercial TiO_2 paste for screen-printing was obtained from JGC CO., Ltd.