Solar Energy 169 (2018) 249–254

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Fast and controllable sensitization of dye-sensitized solar cells by microwave irradiation

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ARTICLE INFO

Keywords:
Dye-sensitized solar cells
Sensitization
Microwave irradiation

ABSTRACT

The unique features of dye-sensitized solar cells (DSCs) with low-cost, easy-assembly, and nature-friendly benefits make them suitable for renewable energy. However, the adsorption of dye on porous TiO_2 surface, usually conducted by a long time immersion (16–24 h) to offer an optimized dye adsorption condition, is a time-consuming process, which inevitably limits their potential in production capacity and throughput. Accordingly, developing a simple route to reduce the dye adsorption process is urgently required. Herein, we present a facile, rapid, efficient sensitization route for efficiently controlling the adsorption of N719 dye on TiO_2 via microwave irradiation for the first time in this work. The dye adsorption condition on TiO_2 can be easily tuned with the number of microwave times and the microwave duration via the microwave-induced thermal effect. Our result reveals that the conversion efficiency of DSCs after the microwave treatment in a short time can be significantly increased, leading to 43% improvement in the conversion efficiency as compared with that without microwave treatment.

1. Introduction

Since a prototype of efficient dye-sensitized solar cells (DSCs) proposed by O'Regan and Grätzel (1991), a simple architecture of a dye-adsorbed TiO_2 photoanode, electrolyte of iodide/triiodide redox, and platinized counter electrode has been embraced to be offered with the low-cost, easy-assembly, and nature-friendly advantages. The DSCs, different from the conventional crystalline silicon solar cells, inherently featured as the semi-transparency, colorfulness, and excellent performance under the low light intensity, further exhibiting the promise for the emergence of practical applications on building-integrated photovoltaics (BIPV) and low power consumer electronics (Heiniger et al., 2013; Kim et al., 2017; Wang and Wu, 2012; Yuan et al., 2018; Yun et al., 2018). Accordingly, while previous research efforts had been made on pursing a higher efficiency, the increase in the productivity of DSCs has been paid much attention recently with more potential applications occurred.

The whole fabrication process of DSCs can be mainly split into TiO_2 synthesis, the dye adsorption, and Pt counter electrode (Hagfeldt et al., 2010). Among them, the dye adsorption process plays a crucial role in attaining an efficient DSC because of its key responsibility for the light absorption and the injection of carrier into the TiO_2 under the illumination. Accordingly, in order to obtain not only an adequate dye loading but also a desirable dye adsorption condition on the TiO_2, the general process of dye adsorption on TiO_2 has to be conducted carefully by a long time immersion (16–24 h) in a dye solution. Unfortunately, this kind of dye uptake process is considered a time-consuming and costly step in DSC fabrication, which inevitably reduces the production capacity and throughput during the manufacturing.

A few methods for improving the dye soaking process were proposed. It is known that the time for the adsorption of the dyes on TiO_2 surface can be decreased by surface modification of TiO_2 via acidic solution (Kim et al., 2013), heated dye solution (Yeh et al., 2015) or a swift uptake/supply procedure performed with the instruments. For instance, Seo et al. provided an external electric field for towing more ionized dyes toward the TiO_2 (Seo et al., 2010). Seo et al. applied a bath-type ultrasonic device to offer the versatile functions of efficiently dispersing the agglomerated dye, penetrating the dye, and releasing the entrapped gases during the dye adsorption (Seo and Kim, 2013). Holliman et al. reported a rapid supply of the dyes to TiO_2 by the circulation system controlled via a pump (Holliman et al., 2010). Han et al. and Hashmi et al. presented an ultrasonic spraying and inkjet printing, respectively, to facilitate the supply of the dye adsorption process (Han et al., 2015; Hashmi et al., 2016). Though these methods can be provided with the advantage of reducing the dye adsorption process, either the precisely controllability of dye utilization and adsorption condition in a short time remain a challenge or these instruments based on a complex design cannot be easy to be realized during the manufacturing.

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https://doi.org/10.1016/j.solener.2018.04.064
Received 24 March 2018; Received in revised form 26 April 2018; Accepted 30 April 2018

Microwave irradiation, known as a non-contact treatment technology, is allowed for the fast, precisely controlled, and selective heating without induced temperature gradient in different applications because of its working principle stemming from the oscillation of the dipoles under the external field (Cao et al., 2016; Fujii et al., 2015; Liu et al., 2017; Pinto et al., 2017; Reeja-Jayan et al., 2012). Recent studies have demonstrated its promising application suitable not only for the synthesis of metal oxide film sintering but also for the integration in a roll-to-roll process, bringing great benefits of DSC manufacturing (Maitani et al., 2013; Maitani et al., 2016; Ullattil and Periyat, 2017). These interesting results motivate us to explore the possibility of microwave irradiation on the adsorption of the dye on TiO_2, which remains missing but highly potential for promoting the productivity. Thus, we developed a facile, rapid, efficient sensitization route for controlling the adsorption of N719 dye on TiO_2 via microwave irradiation for the first time. Different from other dye adsorption approaches, this simple route can provide the possibility of effectively improving the utilization of costly dye and simultaneously integrating into the manufacturing with ease while achieving the required result of the dye adsorption in a short time.

2. Experimental section

2.1. Preparation of TiO_2 photoanodes

Fluorine doped tin oxide (FTO) glasses (7 Ω per square, Ruilong) were sequentially cleaned in an ultrasonic bath for 5 min with detergent, deionized water, acetone, and isopropyl alcohol, followed by a blow dry with nitrogen. The mixed solution of blocking layer TiO_2 (bl-TiO_2) precursor composed of titanium isopropoxide (Merck) and ethanol (Echo) was deposited on the as-cleaned FTO substrate by spin coating method at 2000 rpm for 60 s, followed by a heat treatment of 120 °C for 5 min on a hot plate and then sintered at a tubular furnace of 500 °C for 30 min. Subsequently, the substrate was deposited with the mesoporous TiO_2 (mp-TiO_2) on top of bl-TiO_2. The targeted thickness (~15 μm) of the mesoporous TiO_2 was obtained with several times of the doctor blade coating using a home-made TiO_2 slurry composed of 1*g* of P25 powder (21 nm, Uniregion Bio-tech), 0.2 mL of acetic acid (Sigma-Aldrich), 3*g* of terpineol (Acros), 0.5*g* of ethyl cellulose (CPS200, Aencore), and 10 mL of ethanol. Subsequently, the as-deposited mp-TiO_2 film was sintered at a tubular furnace with a heating profile of 325 °C for 5 min, 375 °C for 5 min, 425 °C for 5 min, and 500 °C for 30 min. The sintered mp-TiO_2 substrate was then soaked with 40 mM $TiCl_4$ solution (Showa) at 68 °C for 30 min, followed by a slowly rinse of ethanol and then a heating treatment at a tubular furnace of 500 °C for 30 min before the dye adsorption process.

2.2. Microwave irradiation processes

The placement and the size of all the samples in the microwave oven (AKM2064ES, Whirlpool) was kept the same to prevent the deviation of microwave distribution each run during microwave treatment. The solution of 10 mM N719 dye was prepared by D719 (Eversolar) and ethylene glycol (EG) (J.T. Baker). Afterwards, the as-prepared sample of mp-TiO_2/bl-TiO_2/FTO (with exposed FTO areas covered with kapton tapes to avoid the direct contact from the solvent) was mildly dripped with 10 μL of 10 mM N719 EG dye solution, followed by microwave irradiation treatment at an output power of 140 W for different microwave durations several times. To keep the concentration of the EG dye solution constant and fresh, 10 μL of 10 mM N719 EG dye solution after microwave treatment was cooled for 30 s before removal and reloaded again each run. The sample after the microwave irradiation treatment was soaked in the ethanol at 40 °C for 5 min to remove the residue of the EG. For the comparison, the control sample was immersed in a 10 mM N719 solution, prepared by D719 and a mixed solvent composed of acetonitrile (Acros) and *tert*-butyl alcohol (Alfa Aesar) with 1:1 in volume ratio or EG, for 20 h.

2.3. Preparation of Pt counter electrodes

The FTO glasses (7 Ω per square, Ruilong) were firstly cleaned as above-mentioned. Subsequently, the sample of Pt counter electrode was synthesized with a 5 mM H_2PtCl_6 solution onto a FTO substrate, followed by a heat treatment at 400 °C for 10 min. A 5 mM H_2PtCl_6 solution was prepared by the mixture of isopropyl alcohol (Acros) and $H_2PtCl_6{\cdot}6H_2O$ (Alf).

2.4. Assembly of DSCs

The DSCs were assembled with a sandwich structure of dye-adsorbed TiO_2 photoanode and Pt counter electrode using commercially available iodide-based liquid electrolyte Eversolar EL-200 in between (Ruilong Optical, Taiwan) with methoxypropionitrile as a solvent. Afterwards, the current density-voltage measurement under AM 1.5 G illumination were performed by Keithley 2000 digital multimeter to obtain the conversion efficiency of DSCs with a defined area of 0.09 cm^2.

2.5. Characterization of materials

To obtain the amount of the dye on TiO_2, the samples after different microwave irradiation treatments were desorbed in 0.1 M NaOH aqueous solution. This collected dye solution was measured with a Hitachi U-4100 UV–Visible-NIR Spectrophotometer and calculated the amount of the dye adsorption on TiO_2 from the intensity of the absorption at 528 nm in terms of the Beer-Lambert Law (Seo and Kim, 2013). To exam the functional groups of the dye adsorption on TiO_2 after different dye adsorption processes, the spectra of attenuated total reflection fourier-transform infrared spectroscopy (ATR-FTIR) for all the samples were performed with Bruker Vertex 70 V equipped with Hyperion 3000 imaging system. To study the penetration of the dye in the TiO_2 after microwave irradiation, the samples with ~4 μm TiO_2 thickness were prepared for detecting the signal of Ru as a function of the depth by time-of-flight secondary ion mass spectrometer (IONTOF).

3. Results and discussion

3.1. Development of microwave irradiation for dye-adsorbed TiO_2

Fig. 1a illustrates the schematic diagram of our developed method utilized for the exploration of the adsorption of the dye on TiO_2 under microwave irradiation. The solution of N719 dye, dissolved in a high microwave absorptivity of EG solvent, is allowed to serve as a versatile medium to provide the functions of both absorbing the microwave energy and delivering the dyes among the TiO_2 during the dye adsorption step of DSC assembly. Accordingly, as the samples of TiO_2/FTO were mildly dripped with a small amount of EG dye solution, the adsorption of dye on TiO_2 can be immediately triggered right after microwave irradiation applied. As compared with the conventional immersion commonly required with a large amount of costly dye solution for 20 h dye adsorption as shown in Fig. 1b, the microwave route can be figured out to provide more benefits in a short time basis for precisely controlling the dye adsorption while effectively improving the utilization of the costly dye. The photographs of the samples after the microwave treatment, as shown in Fig. S1, reveal a uniform distribution of colourful dyes adsorbed on TiO_2, further presenting its possibility for giving a uniform treatment for the dye adsorption process during the manufacturing.

3.2. The influence of microwave irradiation on dye adsorption

To investigate the effect of microwave irradiation on dye