Journal of Power Sources 324 (2016) 637–645

Contents lists available at ScienceDirect

Journal of Power Sources

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

Structural color-tunable mesoporous bragg stack layers based on graft copolymer self-assembly for high-efficiency solid-state dye-sensitized solar cells

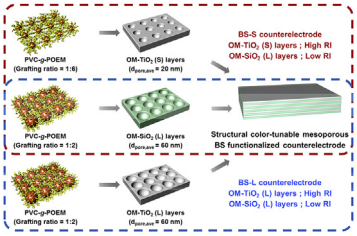
Chang Soo Lee [a], Jung Tae Park [b, *], Jong Hak Kim [a, **]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea
[b] Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea

HIGHLIGHTS

- Structural color-tunable mesoporus Bragg stacks counter electrodes were prepared.
- BS layers were prepared *via* the alternating deposition of OM-TiO_2 and OM-SiO_2 layers.
- The OM layers with controlled *RI* are templated with amphiphilic graft copolymers.
- DSSC with mesoporous BS layer exhibited enhanced cell performance.
- High efficiency (7.1 %) is due to the higher light harvesting.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2015
Received in revised form
21 May 2016
Accepted 27 May 2016

Keywords:
Dye-sensitized solar cells (DSSC)
Bragg stacks
Mesoporous SiO_2
Mesoporous TiO_2
Polymerized ionic liquid

ABSTRACT

We present a facile fabrication route for structural color-tunable mesoporous Bragg stack (BS) layers based on the self-assembly of a cost-effective graft copolymer. The mesoporous BS layers are prepared through the alternating deposition of organized mesoporous-TiO_2 (OM-TiO_2) and -SiO_2 (OM-SiO_2) films on the non-conducting side of the counter electrode in dye-sensitized solar cells (DSSCs). The OM layers with controlled porosity, pore size, and refractive index are templated with amphiphilic graft copolymers consisting of poly(vinyl chloride) backbones and poly(oxyethylene methacrylate) side chains, *i.e.*, PVC-*g*-POEM. The morphology and properties of the structural color-tunable mesoporous BS-functionalized electrodes are characterized using energy filtered transmission electron microscopy (EF-TEM), field emission-scanning electron microscopy (FE-SEM), spectroscopic ellipsometry, and reflectance spectroscopy. The solid-state DSSCs (ssDSSCs) based on a structural color-tunable mesoporous BS counter electrode with a single-component solid electrolyte show an energy conversion efficiency (η) of 7.1%, which is much greater than that of conventional nanocrystalline TiO_2-based cells and one of the highest values for N719 dye-based ssDSSCs. The enhancement of η is due to the enhancement of current density (J_{sc}), attributed to the improved light harvesting properties without considerable decrease in fill factor (*FF*) or open-circuit voltage (V_{oc}), as confirmed by incident photon-to-electron conversion efficiency (IPCE) and electrochemical impedance spectroscopy (EIS).

* Corresponding author.
** Corresponding author.
E-mail addresses: jtpark25@konkuk.ac.kr (J.T. Park), jonghak@yonsei.ac.kr (J.H. Kim).

http://dx.doi.org/10.1016/j.jpowsour.2016.05.129
0378-7753/

1. Introduction

Considering the current shortage of fossil fuels and global warming, highly efficient energy conversion devices are in high demand. Dye-sensitized solar cells (DSSCs) reported by the Gratzel group possess many advantages compared to conventional silicone solar cells, such as low fabrication cost, environmental safety, and utilization as transparent window materials [1]. There are a few major components of DSSCs that have been widely researched, such as photoanodes with a metal oxide layer (TiO_2, ZnO and etc.), ruthenium-based dye sensitizer [2–4], I^-/I_3^- redox electrolyte [5,6], and counter electrodes [7,8]. Most photoanodes and counter electrodes have been deposited onto the transparent conducting oxide (TCO) substrate *via* doctor-blade or spin-coating methods. The TCO substrate, such as fluorine-doped tin oxide (FTO) conductive glass, possesses an important advantage of high transmittance of light in the ultraviolet (UV)-visible region in order to allow light to penetrate into devices and excite electrons in dye molecules [9,10]. However, when TCO is used as a counter electrode material, its high transparency limits the efficient trapping of light back into devices, thereby leading to lower light harvesting.

One approach to increase the light harvesting property is deposition of a functional scattering layer on the nanocrystalline TiO_2 bottom layer. It is well known that the light harvesting properties of TiO_2 composites 200–500 nm in diameter are greater than those of commercially available nanocrystalline TiO_2 (e.g., P25) that is 20–30 nm in diameter [11]. For example, a spherical TiO_2 structure has been shown to not only improve light harvesting, but also to increase dye-loading [12–14]. Nanoporous TiO_2 hollow spheres were also introduced to enhance light harvesting in DSSCs [15–19]. Our group recently introduced the hetero-nanostructure consisting of TiO_2 nanosheets on SnO_2 hollow spheres for solid-state dye-sensitized solar cells (ssDSSCs) [20].

Research on one-dimensional (1D) structures has been widely conducted to achieve both fast electron transport and increased light harvesting. For example, a vertically aligned TiO_2 nanowire or nanorod array on a substrate was employed as a photoanode to offer a direct electron path to maximize the electron transport rate and minimize the charge recombination [21–23]. Moreover, functional 1D TiO_2 nanotube-based photoanodes were prepared in order to improve dye loading and electron transport [24–26]. Our group also reported 1D pine tree-like TiO_2 nanotube arrays and 1D TiO_2 nanosheets on SnO_2 nanotube structures based photoanodes to enhance the light harvesting properties of ssDSSCs [27,28]. 1D photonic crystal-based photoanodes (Bragg Stack, BS) in DSSCs have also been suggested to provide superior light-harvesting properties in target wavelength regions [29–34]. However, these 1D structures based photoanodes have a disadvantage in terms of dye loading, because the specific surface area of such structures is not sufficient to adsorb a large amount of dye sensitizer.

Although improved light harvesting properties have been reported, these DSSCs utilize functional scattering layers, which present limitations such as increased charge recombination at the photoanode/electrolyte interfaces, incomplete penetration of electrolytes, and negative impact on dye degradation [35]. Also, most of the functional scattering layers of incorporated photoanode systems have an opaque white color that is not appropriate for building integrated photovoltaics (BIPV). In this regard, one attractive approach to enhancing light harvesting properties without any side effects is to introduce transparent 1D photonic crystal structures (Bragg Stack, BS) on the outside of counter electrodes. On the other hand, the BS layer on conduction side of counter electrode could potentially lead to problems such as increased charge recombination caused by the presence of an insulating material such as SiO_2, which would result in a lower open circuit voltage (V_{oc}), according to our previous work [36]. Therefore, this novel way has the beneficial effect of improving the probability that nonabsorbed photons will be harvested, which will further increase the photovoltaic performances without the detrimental side effects on electrochemical processes.

SiO_2 nanomaterials have attracted considerable attention and have become an increasingly important interdisciplinary research field in drug delivery, imaging, catalysis and energy device [37–40]. The use of conventional SiO_2 nanomaterial as the low refractive index layer of TiO_2/SiO_2 based 1D photonic crystal structures (Bragg Stack, BS), however, have some limitations in achieving high reflection properties with a low number of layers. Because it is not easy to control of the ratio between SiO_2 and air regions, which limit the refractive index (*RI*) of dense layers based on conventional SiO_2 nanomaterials. One way to overcome the drawback of using dense SiO_2 layers for TiO_2/SiO_2 based 1D photonic crystal structures (Bragg Stack, BS) is to prepare organized mesoporous SiO_2 with tunable optical properties. Recently, the synthesis of macroporous SiO_2 layers using PMMA latex nanoparticles and the silica sol was investigated for a-Si:H solar cells [41]. And, tri-block copolymer (Pluronic P123) templated mesoporous Bragg reflectors were prepared by multiple casting of mesoporous TiO_2 and SiO_2 layers [31]. In this regard, graft copolymers templates are more attractive than block copolymers due to their low cost and ease of preparation. Also, our work is the first report describing the use of mesoporous Bragg Stack layers based on organized mesoporous-TiO_2 (OM-TiO_2) and -SiO_2 (OM-SiO_2) layers.

In this report we present the preparation of structural color-tunable mesoporous Bragg stack (BS) layers templated by an organized graft copolymer, poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate) (PVC-*g*-POEM), as a structure-directing agent. The mesoporous BS layers were prepared through alternating deposition of organized mesoporous-TiO_2 (OM-TiO_2) and -SiO_2 (OM-SiO_2) layers on the non-conducting side of the counter electrode in dye-sensitized solar cells (DSSCs) in order to enhance light harvesting properties. The OM layers were synthesized *via* a sol-gel reaction using PVC-*g*-POEM as templates. The refractive index of OM layers was tuned by controlling the grafting ratio of amphiphilic graft copolymers. Furthermore, we demonstrated that the structural color properties can be tuned *via* refractive index and thickness. The enhancement in the light harvesting properties of DSSCs through incorporation of the mesoporous BS counter electrode was characterized using transmission electron microscopy (TEM), field emission-scanning electron microscopy (FE-SEM), spectroscopic ellipsometry, and reflectance spectroscopy. The performances of quasi-solid-state DSSCs (qssDSSCs) and ssDSSCs were investigated by measuring current density-voltage (*J–V*) curves, incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS). To the best of our knowledge, our report is the first work describing the use of OM-TiO_2 and OM-SiO_2 layers as structural color-tunable mesoporus BS functionalized counter electrodes in DSSCs. Specifically, there is no previous report regarding the OM-SiO_2 layer with small wall thickness and large pore size (>50 nm).

2. Experimental section

2.1. Materials

Poly(vinyl chloride) (PVC, M_w = 97,000 g mol^{-1}, M_n = 55,000 g mol^{-1}), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, M_n = 475 g mol^{-1}), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), titanium (IV) isopropoxide (TTIP, 97%), hydrochloric acid (HCl, 37%), (3-