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Facile, Nonhydrothermal, Mass-Producible Synthesis of Mesoporous TiO_2 Spheres for Dye-Sensitized Solar Cells

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ABSTRACT

We report a facile, non-hydrothermal (or non-solvothermal) and mass-producible synthesis of mesoporous TiO_2 spheres (MTSs) suitable for use in dye-sensitized solar cells (DSSCs). The synthesis is a facile bulk calcination in which the inexpensive polymer ethyl cellulose (EC) is used as a structure-directing agent; the EC concentration is controlled to induce spherical morphology. The size of MTSs can be adjusted by tuning the solute–solvent interactions; for example, the addition of the poor solvent toluene to the solute resulted in the formation of smaller MTSs. A DSSC fabricated using a polymer electrolyte containing ionic liquid and iodine (I_2) and using a layer of MTSs on a nanocrystalline (NC) TiO_2 layer exhibited an efficiency of up to 6.3%, which is much higher than those of DSSCs with an NC layer only (5.0%) or with a commercial scattering layer (CSL) on an NC layer (5.7%). A solid-state DSSC (ssDSSC) using a single component solid polymer, namely poly((1-(4-ethenylphenyl) methyl)-3-butyl-imidazolium iodide) (PEBII), also exhibited an excellent efficiency of up to 6.4%. The improved efficiency was due to the role of the MTSs in improving surface area and light harvesting properties, as demonstrated by N_2 adsorption/desorption isotherm, UV-visible light absorption, reflectance spectroscopy, incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS) analyses.

1. Introduction

Solar cells or photovoltaic cells have attracted a great deal of research attention because of the problems posed by the use of fossil fuels, including carbon dioxide production and shortage of fuel supplies. In particular, dye-sensitized solar cells (DSSCs) have become an attractive technology as an alternative to conventional silicon solar cells due to their low-cost, simple fabrication process, their high efficiency, and the possibility of future improvements [1]. Most DSSCs researches have focused on improving efficiency by modifying dyes [2–6], electrolytes [7–11], counter electrodes [12–16], and TiO_2 photoanodes [17–20]. Among these components, the TiO_2 photoanode has been widely researched, including efforts to enhance its dye loading, light scattering, and electrolyte penetration [17–24]. To enhance the energy conversion efficiency of DSSCs, it is important to utilize the light efficiently and to increase dye loading by developing a micron-sized, mesoporous, large-surface-area metal oxide structure.

Typically, DSSCs are composed of fluorine-doped tin oxide (FTO) glass, a thin TiO_2 blocking layer to prevent recombination, a nanocrystalline (NC) TiO_2 layer, an electrolyte, and a counter electrode that catalyzes the I_3^-/I^- redox couple. However, NC layers based on particles less than 20 nm in size have the critical disadvantage of poor light scattering ability relative to micron-sized nanoparticles. Accordingly, nanorods- and nanotube-based photoanodes have been studied as a means to improve the light scattering ability and electron transport behavior of photoanodes, and have been prepared by various methods such as electro-spinning, hydrothermal synthesis, and electrochemical synthesis [25–29]. Dual-functional mesoporous TiO_2 spheres with high surface area are considered to be highly efficient due to their considerable dye loading ability and excellent light scattering [30–36]. An electrospray method has been employed to synthesize TiO_2 solid spheres and hollow spheres with significant surface area [30]. Also, mesoporous anatase TiO_2 beads have been synthesized by means of a hydrothermal method using amphiphilic graft copolymer templates to generate pores in the hydrophobic domain, and DSSCs based upon these beads and solid-state electrolytes exhibited 6.7% efficiency [32]. As such, the synthesis of mesoporous TiO_2 spheres generally involves hydrothermal or solvothermal methods to require high temperatures and long

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reaction times [31–38], and thus non-hydrothermal, energy-saving method is highly needed.

Despite the high energy conversion efficiency of DSSCs based on a liquid electrolyte, solid-state DSSCs (ssDSSCs) or quasi-solid-state DSSCs have recently received great attention due to the need for long-term stability, flexible design, and lightweight cells [39–43]. One important consideration for ssDSSCs is to obtain good pore-filling of large molecular volume solid electrolytes into the TiO_2 photoanode, which is largely dependent upon the pore structure and pore size. Despite recent progress in incorporating solid or quasi-solid electrolytes, there have not been extensive efforts to enhance the device performance of ssDSSCs by modifying photoanode structures. Furthermore, for future applications such as building integrated photovoltaics, ssDSSCs with enhanced energy conversion efficiency as well as long-term stability need to be developed.

In this work, we first report a facile, non-hydrothermal (or non-solvothermal), and mass-producible synthesis of MTSs for ssDSSCs applications. The method comprises a facile bulk calcination with ethyl cellulose (EC), an inexpensive polymer, based on the control of the EC concentration above a critical aggregation concentration. The MTSs synthesized were employed to form top scattering layers on NC-TiO_2 layers for use in ssDSSC applications, and these MTS layers were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), N_2 adsorption–desorption isotherm analysis, UV-visible light absorption and reflectance spectroscopy. The performances of DSSCs were investigated by measuring current density–voltage (J-V) curves, incident photon-to-current efficiency (IPCE) and electrochemical impedance spectroscopy (EIS).

2. Experimental section

2.1. Materials

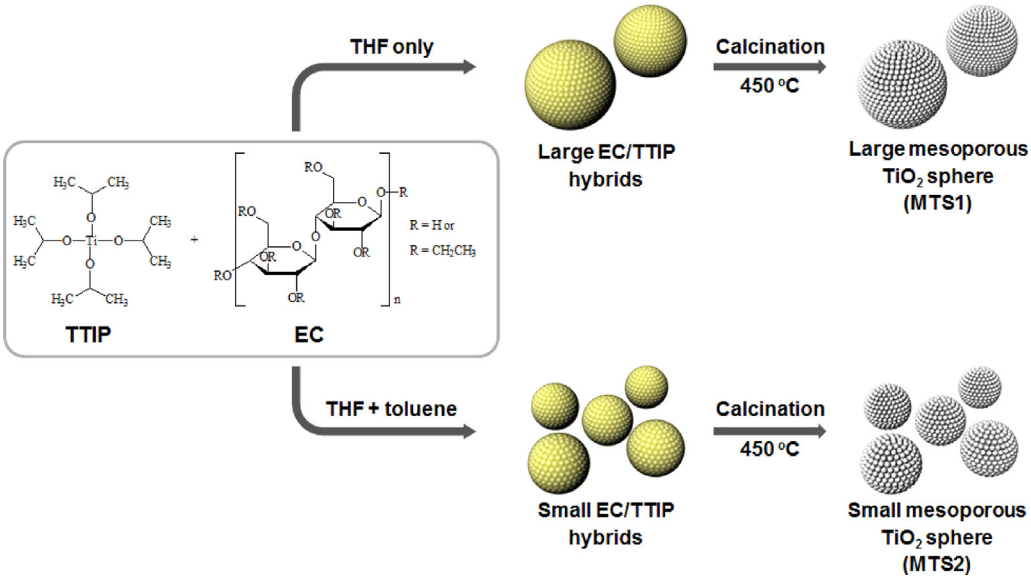
EC (viscosity 22 cP, 5% in 80:20 toluene/ethanol), titanium (IV) isopropoxide (TTIP, 97%), titanium diisopropoxide bis(acetylacetonate) (75 wt.% in isopropanol, Aldrich), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, ≥37.50% Pt basis, Aldrich), hydrochloric acid (HCl, 37%), 1-methyl-3-propylimidazolium iodide (MPII, ≥98.0%), poly(ethylene glycol) (PEG, M_n = 10,000 g/mol), iodine (I_2, ≥99.99%), and lithium iodide (LiI, 99.9%) were all purchased from Aldrich, and were used as received without any purification or treatment. Tetrahydrofuran (THF, 99.5%) was purchased from Daejung Chemicals, and toluene (≥99.5%), acetonitrile (≥99.9%), and alcohol (anhydrous, reagent-grade) were purchased from J.T. Baker; all of these solvents were used as received without any purification. Ruthenium dye (535-bisTBA, N719) was purchased from Solaronix, and commercially available TiO_2 paste (Dyesol paste, 18NR-T) was purchased from Dyesol. FTO conductive glass was purchased from Pilkington, France.

2.2. Bulk calcination synthesis of MTSs

EC of 1.5 g was dissolved in 12 ml of THF only or in a 10 ml/2 ml mixture of THF/toluene to make a viscous and transparent polymer solution. Titania sol–gel solution was prepared according to a previously reported method [41–43]. Briefly, HCl was slowly dropped into TTIP under vigorous stirring and the solution was further stirred for 30 min to produce a transparent yellowish sol–gel solution. As-prepared sol–gel solution of 2.25 ml was added into the polymer solution under stirring and was aged for 24 h to obtain a homogeneous solution. To remove solvents, the solution was placed in a drying oven at 50 °C for 24 h, followed by drying in a vacuum oven at 50 °C overnight; the dried material was then annealed at 450 °C for 2 h to remove organic compounds. Two kinds of samples were obtained by using the THF solvent and the 10 ml/2 ml solvent mixture of THF/toluene; these samples were respectively designated MTS1 and MTS2. With the above synthesis condition, approximately 0.4 g of MTS powder was obtained. Also, it was possible to produce more MTS nanoparticles by multiplying the amount of reactants up to 4.5 g of EC with the same conditions.

2.3. Preparation of photoanodes

First, FTO glass substrates were serially washed with ethanol, with acetone, and again with ethanol, for 30 min each under sonication. To block electrolyte-mediated recombination at the surface of the FTO glass, it was covered with a thin TiO_2 layer by spin-coating 5 wt.% of titanium diisopropoxide bis(acetylacetonate) in 1-butanol onto the washed FTO glass at 1500 rpm for 20 s, and annealed at 450 °C for 30 min. Highly viscous, commercially available Dyesol paste was doctor bladed onto the blocking layer, dried at 120 °C in an oven, and annealed at 450 °C for 30 min to prepare a transparent, 6-μm-thick NC-TiO_2 layer. To prepare highly viscous MTS paste



Scheme 1. Synthesis of different-sized MTSs from EC/TTIP hybrid precursors by controlling solute–solvent interactions.