



Enhanced charge collection in dye-sensitized solar cells utilizing collector–shell electrodes



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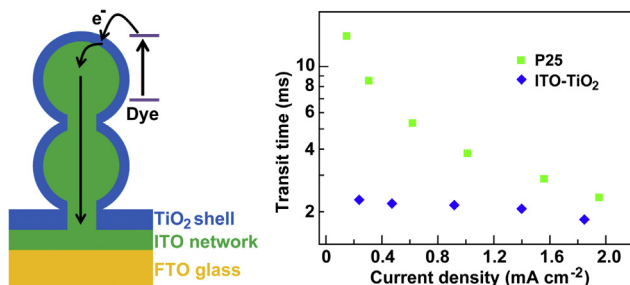
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HIGHLIGHTS

- ITO–TiO₂ collector–shell electrodes prepared by screen-printing and TiCl₄ treatment.
- DSCs using these electrodes exhibit a best power conversion efficiency of 3.3%.
- Charge transport is fast in DSCs utilizing the collector–shell electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured porous tin-doped indium oxide (ITO) films were prepared by screen printing of an ITO nanoparticle paste onto conducting fluorine-doped tin oxide (FTO) substrates. The ITO films were subsequently coated with thin layers of TiO₂ by the hydrolysis of TiCl₄ to form the collector–shell photoelectrodes. The morphology of films was analysed by scanning electron microscope (SEM). It was found that a uniform coating of TiO₂ was achieved when three or more deposition cycles were applied. Dye-sensitized solar cells were constructed with the collector–shell photoelectrodes using an electrolyte containing the [Co(bpy)₃]^{2+/3+} (bpy = 2,2'-bipyridine) redox couple and MK-2, an organic sensitizer and efficiencies of 3.3% achieved. Charge transport in cells utilizing the collector–shell electrodes was found to be 2–6 times faster than those utilizing P25-based TiO₂ electrodes.

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1. Introduction

The dye-sensitized solar cell (DSC) has received great attention in recent years as a promising photovoltaic technology for producing clean and renewable energy [1–5]. The ease of fabrication and cost-effectiveness of DSCs as well as the good power

conversion efficiency of 13% have made them promising candidates for renewable energy applications [6–11]. A classical DSC device consists of a dye-sensitized mesoporous semiconductor film as working electrode, an electrolyte containing a redox mediator and a platinum coated conductive glass as counter electrode [6]. Under illumination, photoexcitation of the dye molecules results in the injection of excited electrons into the semiconductor conduction band. These photoexcited electrons then have to undergo numerous trapping and detrapping events at defect states within the randomly oriented nanoparticulate network before finally

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reaching the current collector [12]. During this process, charge recombination at the substrate and/or semiconductor–electrolyte interfaces can occur resulting in a decrease in the charge collection efficiency. Moreover, the structural disorder at the interface of neighbouring nanoparticles usually leads to scattering of free electrons, thereby decreasing electron mobility in the film [13]. Furthermore, when redox couples with fast electron interception rates are utilized, it is important to ensure that the electrons move through the photoanode rapidly to minimize unwanted recombination reactions.

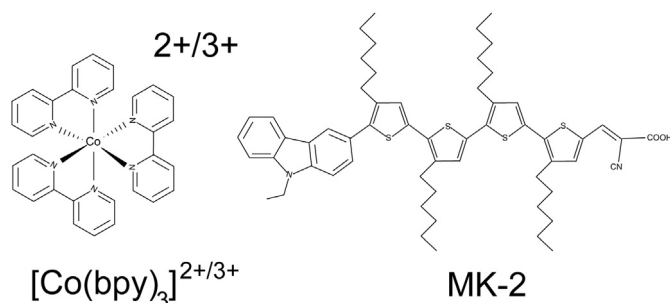
Based on these considerations, two distinct strategies have been proposed to accelerate charge collection in the photoanode. Firstly, electron diffusion in the photoanode can be enhanced by replacing the nanoparticles with one-dimensional crystalline nanostructures [13–17]. Electron transport in one-dimensional crystalline pathways, such as nanowires and nanotubes, has been shown to be much faster than passing through a random polycrystalline network [14]. Moreover, it was also found that the electron lifetime in nanowire or nanotube films can be 3 times longer than in the nanoparticle films [18]. However, films utilizing one-dimensional nanostructures usually have reduced surface areas for dye absorption, which in turn leads to lower photocurrents due to less efficient light harvesting [19]. The second approach is to reduce the electron diffusion length by utilizing the “collector–shell” strategy [20]. A collector–shell electrode consists of a porous scaffold material having high electronic conductivity and a thin metal oxide shell. The shell provides sites for dye adsorption and photoelectron injection while the conductive backbone provides for fast electron transport. The shell thickness can be as thin as tens of nanometers. Therefore, all electrons injected into the electrode, including those that are generated several microns away from the substrate, need only travel across a thin shell before entering the much more conductive backbone where charges can be quickly extracted to the current collector. Furthermore, when a three-dimensional network is used, the morphology and large surface area of the porous scaffolds can be preserved after the semiconductor coating is introduced. Such collector–shell electrodes, in principle, permit a higher dye loading compared to nanowire electrodes. Previously, Grinis et al. reported DSCs constructed with mesoporous ITO–TiO₂ collector–shell electrodes which achieved efficiencies of 1.67% when an additional thin MgO coating was applied on top of the semiconductor [20]. Martinson et al. proposed the concept of the radial electron diffusion in DSCs constructed with concentric ITO–TiO₂ nanotube electrodes, which results in dramatically higher current densities [21]. Noh et al. showed that DSCs fabricated with 3D ITO–TiO₂ core–shell nanowire arrays exhibit extremely fast charge collection properties [22]. Tétreault et al. developed a highly conducting and light scattering photoanode based on TiO₂ coated macroporous Al/ZnO host for DSCs and established an increase in the photovoltage of 110 mV over state-of-the-art DSCs [23]. Very

recently, DSCs with drift-assisted charge extraction were constructed with 3D FTO–TiO₂ core–shell electrodes [24]. Most of these studies have focused on the traditional iodide/tri-iodide redox couple. However, the charge collection efficiencies in these cells are close to unity because of the slow redox chemistry of iodide/tri-iodide redox couple [25]. In sharp contrast, the application of the collector–shell electrodes in DSCs utilizing redox couples with fast electron transfer properties has received much less attention [25].

In this work, we report a facile method to fabricate nanostructured collector–shell photoelectrodes composed of a 3D porous ITO core coated with a thin TiO₂ shell for enhanced charge extraction in DSCs. Solar cells were constructed with a cobalt redox couple ([Co(bpy)₃]^{2+/3+}) and an organic sensitizer MK-2 (Scheme 1). The deposition of thin TiO₂ shells onto porous ITO substrates was achieved through a wet-chemistry sol–gel process, which is better suited for large scale production when compared to previously used vacuum-based deposition techniques [21,23–25]. We demonstrate that charge transport across the porous ITO–TiO₂ collector–shell electrode is much faster than in conventional TiO₂ photoanodes based on the widely used P25 nanoparticles.

2. Experimental

All chemicals were commercially available and used as received unless otherwise specified. The [Co(bpy)₃](TFSI)₂ and [Co(bpy)₃](TFSI)₃ complexes (bpy = 2,2′-bipyridine, TFSI = bis(trifluoromethane)sulfonimide) forming the redox couple were synthesized according to a previous study [26]. The ITO paste for preparing the conductive ITO scaffold was developed by mixing 15 g of an ITO dispersion (<100 nm (DLS), 30 wt% in isopropanol, Sigma Aldrich) with 25 mL of 10 wt% ethyl cellulose in ethanol and 20 mL of terpineol [27]. After a homogeneous mixture was formed, the ethanol was removed on a rotary evaporator to form the paste. The TiO₂ paste for making normal electrode based DSCs was prepared accordingly except that the mixture was composed of 2 g of commercial P25 powder, 16 mL of 10 wt% ethyl cellulose in ethanol and 8.7 mL of terpineol. The glass substrate used was 4 mm thick 10 Ω/□ conductive FTO glass with high transparency in the visible range purchased from Nippon sheet glass. Mesoporous 4 × 4 mm ITO and TiO₂ films were printed using a commercial semi-automatic screen printer with the ITO paste and TiO₂ paste, respectively. Both films were sintered at 500 °C for 30 min after printing. To prepare the ITO–TiO₂ collector–shell electrode, the sintered ITO film was immersed in a 20 mM aqueous TiCl₄ solution and heated at 70 °C for 30 min in a water-saturated atmosphere. The film was dried and again calcined at 500 °C again to crystallize the TiO₂ nanoparticle coating. This process was repeated several times to obtain films with different TiO₂ coating thicknesses. For preparing normal electrode, the sintered TiO₂ film was immersed in a 40 mM aqueous TiCl₄ solution and heated at 70 °C for 30 min. Prior to device assembly, both TiO₂-coated ITO and TiO₂ films were sintered again (500 °C), cooled to approximately 80 °C and immersed in a solution of MK-2 (0.3 mM) in a 1:1:1 mixture of *tert*-butanol, toluene and acetonitrile for 12 h. The dyed films were rinsed with toluene to remove non-attached dye from the films. Counter electrodes were prepared from 4 mm thick 10 Ω/□ conductive FTO glass purchased from Nippon glass. A 10 mM solution of chloroplatinic acid hexahydrate in ethanol was doctor bladed onto the pre-drilled substrate and pyrolysed for 15 min at 450 °C. Electrolytes were prepared using anhydrous acetonitrile, deoxygenated by freeze-drying and stored in a nitrogen glove box. Electrolytes were prepared by mixing [Co(bpy)₃](TFSI)₂ (0.2 M), [Co(bpy)₃](TFSI)₃ (0.07 M), 4-*tert*-butylpyridine (1 M) and LiTFSI (0.05 M) in acetonitrile. The working and counter electrodes were



Scheme 1. Schematic illustration of the cobalt-based redox couple and MK-2 dye.

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