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Experimental and theoretical investigation of dye sensitized solar cells integrated with crosslinked poly(vinylpyrrolidone) polymer electrolyte using initiated chemical vapor deposition

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ABSTRACT

Initiated chemical vapor deposition is used to integrate crosslinked poly(vinylpyrrolidone) (PVP) as a polymer electrolyte into the mesoporous TiO_2 photoanode of dye sensitized solar cells (DSSCs). By adjusting the fractional saturation ratio of ethylene glycol diacrylate (EGDA) crosslinker to vinylpyrrolidone (VP) monomer, the amount of crosslinker within the crosslinked polymer is controlled directly, and a minimum ratio of 0.2:1 (EGDA to VP) is found to form a robust insoluble crosslinked film. Fineman-Ross copolymer analysis indicates that both VP and EGDA prefer to polymerize with VP rather than with EGDA, likely due to reduced steric hindrance. DSSCs incorporating crosslinked PVP polymer electrolyte are found to have 51% higher power conversion efficiency (37% higher in open circuit voltage and 25% higher in fill factor) compared to DSSCs with liquid electrolytes. First-principles macroscopic mathematical modeling reveals that the polymer electrolyte shifts the conduction band of TiO_2 (vs. normal hydrogen electrode) negatively, increases shunt resistance, and affects interfacial processes like back-electron surface recombination in the cell.

1. Introduction

The dye sensitized solar cell (DSSC), first introduced by the Grätzel group in 1991 [1], is a promising photovoltaic technology that has received significant scientific attention due to its lower manufacturing costs compared to conventional silicon-based homojunction solar cells [2], and currently have cell efficiencies of over 14% [3]. A recent renaissance of DSSCs have highlighted that more research needs to be done on the electrolyte medium and on engineering the interface between the TiO_2 and electrolyte to further improve performance and stability [4]. Fig. 1 illustrates the components within a DSSC. It is composed of a mesoporous TiO_2 photoanode coated on a transparent conducting oxide layer such as fluorine-doped tin oxide (FTO) glass [5]. The TiO_2 photoanode is often sensitized with a monolayer of a ruthenium dye, although donor-pi-acceptor organic dyes have also been used [6]. The dye is photoexcited by visible light and injects an electron into the TiO_2. Electrons move, via diffusion, through the TiO_2 photoanode to the FTO, travel through an external load, back to the cell's platinized cathode, and into the electrolyte solution. The electrolyte is typically an organic liquid containing an iodide/triiodide redox couple. The iodide/triiodide redox couple accepts the electrons from the cathode and transports them back to the photoanode to regenerate the dye.

A major limitation of the current DSSC design is the liquid electrolyte, which is prone to leakage and evaporation, and is corrosive to metal contacts such as silver which affect long term stability [7]. Furthermore, electron recombination loss is significant at the TiO_2-electrolyte interface as the photogenerated electrons traveling through the TiO_2 can be captured by the redox electrolyte prior to leaving the cell. Therefore, replacing the liquid electrolyte can enhance DSSC performance, address DSSC stability, and overcome other major issues related with liquid electrolytes. Solid-state alternatives to liquid electrolytes include p-type semiconductors [8], hole conductors [9–11], and polymeric materials incorporating the triodide/iodide redox couple [12,13]. Deposition of these alternatives within the porous TiO_2 layer must be done without degrading or dissolving the dye—therefore without the use of high temperatures. Common methods are casting from solution, vacuum deposition, injection of a polymer solution following by gelation, and dip coatings [12,14]. For instance, poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) has been used to replace the liquid electrolyte in DSSCs [15]. To impregnate the photoanode with the polymer electrolyte, PVDF-HFP was mixed with a liquid electrolyte and heated until no solid was observed, then this hot solution filled the photoanode using a vacuum pump and cooling solidified the solution within the electrode. However, these methods often lead to incomplete poor filling for photoanodes over 2 μm [12,14] and

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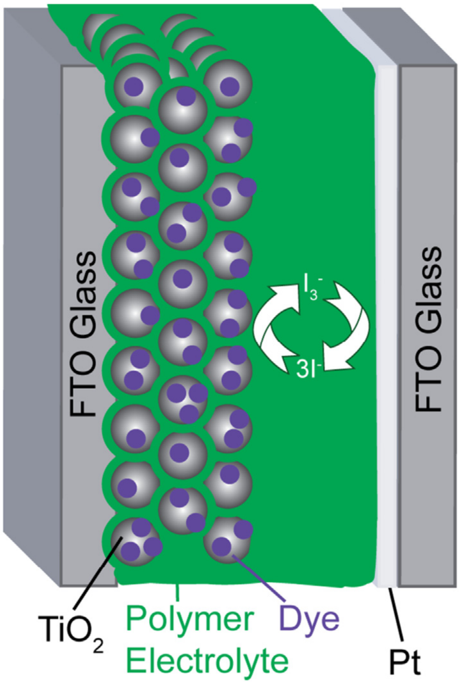

Fig. 1. Schematic of a polymer electrolyte DSSC, including the major components such as the mesoporous network of TiO$_2$ nanoparticles (silver sphere), adsorbed dye molecules (purple circle), polymer electrolyte (green), platinum coated FTO glass (right side), and redox couple of iodide and triiodide (arrows show the redox shuttle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

poor pore filling is the main disadvantage of using organic hole transport materials [14]. Therefore, work has also been done on in-situ photoelectrochemical polymerization, which has led to improved pore filling [14]. Although liquid electrolyte alternatives are being intensely studied, there are currently few studies that combine both experiments and mathematical modeling to better understand the interfacial DSSC processes/interfaces and the interplay between components. Compared to the wide number of experimental DSSC studies, only a few studies mathematically model the DSSC using first principles [7]. Nevertheless, accurate first-principles mathematical models can provide valuable insight and guidance to facilitate future advances in solar technology. In particular, when these models are coupled with experimental results, it allows for the systematic optimization of DSSC design and operation. First-principles macroscopic models, which are based on fundamental continuity and transport equations, can describe overall DSSC behavior and so can work in tandem with experiments [16]. In our previous work, it was shown that replacing the liquid electrolyte with a polymer electrolyte leads to higher performance along with the ability to tune the current-voltage (*J-V*) behavior of the cell [7,17]. Using first-principles mathematical modeling, this increase was attributed to a stabilized and enhanced TiO$_2$ photoanode-electrolyte interface. Moreover, polymer electrolytes have reasonable ionic conductivity, which make them an excellent alternative to the liquid electrolyte [14].

To ensure optimal performing DSSCs, there needs to be intimate contact between the polymer electrolyte and the TiO$_2$ throughout the entire photoanode layer to ensure the redox couple can reach the adsorbed photosensitive dye. A major obstacle of using polymer electrolytes within the nanostructured, high aspect ratio and tortuous mesoporous TiO$_2$ photoanode is the effect of liquid viscosity, surface tension, solute steric hindrance and poor wettability, which leads to ineffective pore penetration using conventional polymer deposition techniques such as spin casting and dip coating from polymer solutions. Often only the top 2 μm out of a 10 μm photoanode layer is in contact with the polymer with the remaining 8 μm below completely void of polymer [8,18–20]. This reduces device performance because a large portion of the adsorbed dye is not accessible to the electrolyte and cannot be regenerated. Many leading DSSC researchers, including Grätzel, have stated that incomplete pore filling is one of the main factors limiting solid-state DSSC efficiency [21]. To overcome the limitation of the methods for incorporating polymer electrolytes into the mesoporous TiO$_2$, we employ a unique polymerization technique called initiated chemical vapor deposition (iCVD) [22,23]. iCVD is a solvent-free, adsorption-limited polymerization method that relies on gas-to-surface reactions at low pressures. This makes it especially useful for cases that require penetration of nanometer-sized pores and allows for uniform conformal coatings in complex geometries [24,25]. Another advantage of this method of deposition for DSSCs is that it does not require the use of any liquid solvents, which may get trapped in the photoanode and degrade performance since they are difficult to remove [17].

In this work, iCVD is utilized for the synthesis and integration of crosslinked poly(vinylpyrrolidone) (PVP) into the mesoporous TiO$_2$ photoanode of DSSCs. We have previously conducted experimental iCVD studies which investigated the kinetics of PVP synthesis and spectroscopically proved the formation of stoichiometric, linear PVP homopolymer using FTIR and X-ray photoelectron spectroscopy [26]. This study first aims to investigate the iCVD deposition behavior of crosslinked PVP using ethylene glycol diacetate (EGDA) as the crosslinker. The second part of this study aims to elucidate the DSSC behavior of crosslinked PVP as the polymer electrolyte. Previous work by our group to incorporate linear polyglycidol (PGL), without a crosslinker, into mesoporous TiO$_2$ illustrated that iCVD can conformally deposit PGL and fill 91% of the available pore space [24]. This works builds on those findings to incorporate two co-monomers, VP and EGDA, into the mesoporous TiO$_2$ photoanode as a crosslinked polymer electrolyte for DSSCs. Uniquely, to investigate the impact of this PVP chemistry on DSSC performance and internal processes, first principles mathematical modeling is used. By combining first-principles modeling with experiments, we gain a better understanding of the interfacial processes occurring inside the DSSCs. The model allows us to predict how PVP's chemistry influences the photochemical processes and *J-V* behavior of the solar cell. Currently, there is little understanding of how this polymer electrolyte affects the internal and interfacial DSSC processes and this study helps to illuminate the possible effects.

2. Experimental details

2.1. iCVD of PVP

Fig. 2 shows the general scheme of the iCVD process. Also shown is the iCVD pore filling process in which the reagents flow into the reaction chamber as vapors which can easily penetrate into the mesoscale voids and polymerize on the pore surface. The reagents flow past a series of heated filament wires whereupon the initiator is thermally decomposed into free radicals without degrading the monomer. Subsequently, monomer vapor adsorbs on a cooled substrate surface and surface polymerization occurs through monomer addition and polymer chain propagation at activated initiator sites. Since PVP was found to dissolve in the redox solvent, crosslinking was introduced to the iCVD polymerization reaction in order to ensure polymer stability and insolubility, as shown in Fig. 3. The monomer 1-vinyl-2-pyrrolidone (VP; 99% Aldrich), initiator di-*tert*-butyl peroxide (TBPO; 98% Aldrich) and crosslinker ethylene glycol diacrylate (EGDA; 98% Alfa Aesar) were used as received. Crosslinked PVP was firstly deposited as a thin film on silicon wafers in order to facilitate initial spectroscopic and microscopic evaluation. For deposition, the monomer VP and crosslinker EGDA were heated in source containers to 90 and 70 °C, respectively, in order to attain sufficient vapor pressure, while initator TBPO was kept at room temperature. The reactor pressure was maintained at

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