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Cellulose Nanocrystal Aerogels as Electrolyte Scaffolds for Glass and **Plastic Dye-Sensitized Solar Cells**

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Supporting Information

ABSTRACT: The fabrication, thickness, and structure of aerogel films composed of covalently cross-linked cellulose nanocrystals (CNCs) and poly(oligoethylene glycol methacrylate) (POEGMA) were optimized for use as electrolyte absorbers in dye-sensitized solar cells (DSSCs). The aerogel films were cast directly on transparent conducting counter electrode substrates (glass and flexible poly(ethylene terephthalate) plastic) and then used to absorb drop-cast liquid electrolyte, thus providing an alternative method of filling electrolyte in DSSCs. This approach eliminates the use of electrolyte-filling holes, which are a typical pathway of electrolyte leakage, and furthermore enables a homogeneous distribution of electrolyte components within the photo-



electrode. Unlike typical in situ electrolyte gelation approaches, the phase inversion method used here results in a highly porous (>99%) electrolyte scaffold with excellent ionic conductivity and interfacial properties. DSSCs prepared with CNC-POEGMA aerogels reached similar power conversion efficiencies as compared to liquid electrolyte devices, indicating that the aerogel does not interfere with the operation of the device. These aerogels retain their structural integrity upon bending, which is critical for their application in flexible devices. Furthermore, the aerogels demonstrate impressive chemical and mechanical stability in typical electrolyte solvents because of their stable covalent cross-linking. Overall, this work demonstrates that the DSSC fabrication process can be simplified and made more easily upscalable by taking advantage of CNCs, being an abundant and sustainable bio-based material.

KEYWORDS: cellulose nanocrystals, CNC, aerogels, dye-sensitized solar cell, DSSC, flexible photovoltaics, gel electrolyte, electrolyte scaffold

INTRODUCTION

Photovoltaics is the world fastest growing energy technology. The aim is that of meeting the growing energy demand and reducing the emission of greenhouse gases from fossil fuels. The European Joint Research Centre estimates that solar energy could supply 20% of the world energy consumption by 2050 and over 50% by 2100.1 Dating back to the development of the first crystalline silicon solar cell in 1954 from Bell Laboratories, the widespread use of photovoltaics has been limited due to high manufacturing and environmental costs.^{2,3} A newer development of photovoltaic technology is the dyesensitized solar cell (DSSC). First introduced in 1991 by

Grätzel and O'Regan, the DSSC has advantages over traditional solar cell designs (e.g., monocrystalline silicon) such as low cost and ease of fabrication due to the variety of suitable materials and preparation methods.^{4,5} For large-scale production, it is crucial to replace scarce and expensive materials with abundant, cost-effective, degradable, and environmentally friendly alternatives.^{6,7} Recently, there has been increased interest in the utilization of natural materials,

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such as wood and biowaste, in photovoltaics.⁸ Renewable materials have been incorporated in various photovoltaic components, including substrates,^{9–11} photoelectrode supports,¹² dyes,^{13,14} electrolyte gelators,¹² catalysts,^{13,15,16} and optical layers to improve light absorption.^{17,18}

Standard DSSCs utilize an I^-/I_3^- redox electrolyte dissolved in organic solvent-typically acetonitrile (ACN) or 3methoxypropionitrile (3-MPN).³ Despite producing the highest efficiencies, liquid electrolytes have drawbacks such as difficulties in sealing and constructing large modules and tandem structures. Liquid electrolytes are also known to leak or evaporate, corrode the counter electrode and sealing materials used in large-scale production, and cause dye desorption from TiO₂, resulting in poor long-term stability.^{3,19} A popular approach is to replace the liquid electrolyte with a solid or quasi-solid-state material. These often include the use of p-type semiconductors, solid polymer electrolytes, or gel polymer electrolytes. Solid polymer electrolytes solve issues associated with liquid electrolytes. However, their poor ionic conductivity $(10^{-5}-10^{-7} \text{ S/cm})$ results in low power conversion efficiency.²⁰ Thus, quasi-solid gel polymer electrolyte systems have been explored because they have the cohesive properties of solids and the highly conductive (10^{-3}) S/cm) properties of a liquid.²⁰

The fabrication of quasi-solid electrolytes typically involves trapping the liquid electrolyte within the pores of a physically or chemically cross-linked polymeric matrix (e.g., polyacrylate^{21–23} and poly(ethylene glycol)^{24–26} derivatives) or by using low-molecular-mass organic and inorganic gelators.^{27,28} While cross-linked polymeric matrices are mechanically stable and durable, they typically lower the overall efficiency of the device by impeding the diffusion of redox ions and/or hindering charge transfer between the electrode (porous TiO₂ film and counter electrode) and electrolyte, thus increasing overall internal resistance.²³ This is because many reports do not tailor the cross-link density of the matrix to mitigate these effects. Approaches to fabricate self-standing and low-density electrolyte scaffolds are scarce in the literature.²⁹

On the other hand, recent work by Miettunen et al. demonstrated the use of cellulose nanofibril (CNF) aerogels as a quasi-solid electrolyte.³⁰ CNF suspensions were fed into a fluidizer, and the slurry was screen-printed onto the DSSC counter electrode. The gel was instantly frozen by using liquid nitrogen and lyophilized, forming a CNF aerogel with >98% porosity. The liquid electrolyte $(I^-/I_3^- \text{ in } 3\text{-MPN})$ was dropcast onto the aerogel, and the cell was subsequently assembled. The main advantage of using an aerogel in the DSSC fabrication protocol was the elimination of electrolyte-filling holes in the counter electrode, which improved cell encapsulation by eliminating a common pathway of electrolyte leakage. Another significant advantage was that the aerogel was uniformly wetted with the electrolyte, enabling an even distribution of performance-enhancing additives, such as 4tert-butylpyridine (4-tBP) and 1-methylbenzimidazole (NMBI). Conventionally, the electrolyte is injected into the electrolyte-filling holes and laterally pushed through the solar cell. Because the nanoporous photoelectrode can filter electrolyte components, the distribution of electrolyte additives adsorbed on the photoelectrode is therefore nonuniform, causing varying performance at different ends of the device.³¹ The loss of overall performance due to this effect is particularly significant in large-scale devices, where the lateral path of electrolyte movement is much longer.³¹ By use of an aerogel,

the electrolyte is uniformly pressed against the photoelectrode, and the filtering effect with subsequent performance losses can be eliminated. The CNF aerogel had no significant impacts on solar cell performance based on I-V characterization in smallscale devices, showing that it was inert and did not interfere with solar cell performance, which is expected due to the sparsity of the network.³⁰ Electrochemical impedance spectroscopy (EIS) revealed that the aerogel did not block charge transfer between the electrode catalyst/electrolyte interface nor did it hinder electrolyte diffusion.

However, the long-term durability of this material is limited as the CNF network is only held together by physical interactions, resulting in nanofiber dispersion over time.³² In the research presented here, we investigated how the thickness of covalently cross-linked aldehyde-functionalized cellulose nanocrystal (aCNC) and hydrazide-functionalized poly-(oligoethylene glycol methacrylate) (hPOEGMA) aerogels impacts DSSC performance. These aerogels were also fabricated on ITO-coated PET to demonstrate their application toward flexible DSSCs. Compared to previously described CNF aerogels, the materials used here have a welldefined morphology and surface chemistry,³³ thus making it easier to control aerogel properties such as porosity and crosslink density. Furthermore, the applied cross-linking chemistry does not require additional stimuli such as UV, heat, or crosslinking agents and also allows for using milder freezing conditions, thus making the process highly energy efficient. We anticipate that this material with its covalent chemistry can be applied toward upscale roll-to-roll compatible deposition techniques.

EXPERIMENTAL SECTION

Preparation of Aerogel Components. Cellulose nanocrystals (CNCs) were produced through the acid hydrolysis of ashless cotton filter aid (Whatman, GE Healthcare Life Sciences, CAT No. 1703-050, Mississauga, Canada) in 64 wt % sulfuric acid (Caledon Laboratories, Mississauga, Canada) at 45 °C for 45 min.³⁴ The resulting CNCs had surface sulfate half ester groups (sCNCs) and were further functionalized with aldehyde groups (aCNCs) by using a sodium periodate (Sigma-Aldrich, Oakville, Canada) oxidation route as described in prior work.³⁵ The aCNCs generated had a z-average mean particle size of 92 \pm 8 nm determined by dynamic light scattering (DLS, Malvern Zetasizer 3000, Malvern, UK), zeta potential of -16 ± 2 mV (ZetaPlus Zeta Potential Analyzer, Brookhaven Instruments, Holtsville, NY), and an aldehyde functionalization content of $1.56 \pm 0.09 \text{ mmol/g}$ as determined by conductometric titration³⁶ (VWR sympHony). Note that CNCs are rod-shaped, and DLS assumes spherical particles and as such is only used for relative comparison of size and to show good particle dispersion. sCNCs measured in our lab have a z-average mean particle size of 55–85 nm by DLS.^{37,38} hPOEGMA (branched polymer containing 10 mol % oligo(ethylene glycol) methyl ether methacrylate with 8-9 ethylene oxide repeat units, 90 mol % di(ethylene glycol) methyl ether methacrylate with two ethylene oxide repeat units, and 30 mol % hydrazide functionality) was synthesized as previously described.33,3

Fabrication of Aerogel Films on DSSC Counter Electrodes. FTO-coated glass (TEC-15, Pilkington, UK, sheet resistance 15 Ω / sq) and ITO-coated poly(ethylene terephthalate) (PET, sheet resistance 60 Ω /sq) were tested as DSSC counter electrodes. Aerogel films (1 wt % sol–gel concentration, 1:1 aCNC:hPOEGMA weight ratio) were patterned onto the counter electrodes by using a recently developed pressure-aided freeze casting technique.⁴⁰ Briefly, FTO-coated glass was cleaned with piranha solution (5:1 H₂SO₄:H₂O₂ v/v) for 15 min at 110 °C while ITO-coated PET was cleaned by using UV-ozone (Novascane, Boone, IA) for 2 h to remove organic residue.

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A 20 nm thick catalytic Pt layer was sputtered onto the counter electrodes by using a Torr Compact Research Coater CRC-600 manual planar magnetron sputtering system (Torr International, New Window, NY). This thickness was optimized to obtain good charge transfer resistance at the counter electrode/electrolyte interface (R_{CT} 5–30 Ω) throughout the fabrication process. A 7 μ m thick Parylene (Specialty Coating Systems, Indianapolis, IN) or 85 μ m thick adhesive (DU 300, Semiconductor Equipment Corp., Worcester, MA) film was adhered to the counter electrode depending on the desired aerogel thickness. The film was patterned by xurography using a blade cutter (ROBOPro CE5000-40-CRP, Graphtec America Inc., Irvine, CA) to create $5 \times 8 \text{ mm}^2$ molds. Premixed aCNC:hPOEGMA sol-gel suspensions were drop-cast on the mold and immediately frozen at -30 °C while under pressure. The frozen gel was lyophilized, and the mold was subsequently lifted off to reveal the aerogel of desired thickness and pattern. It should be noted that, in contrast to the previously reported method, in this work there was no poly(allylamine hydrochloride) added onto the Pt surface, since it was observed to impede charge transfer at the electrolyte/counter electrode interface. Instead, the Pt surface was cleaned with UVozone to increase surface wettability. Although UV-ozone treatment can degrade the Pt surface, the 20 nm thickness is sufficient to withstand this. In fact, UV-ozone degradation increases the Pt surface roughness, which can improve electrolyte charge transfer due to an increase in surface area.⁴¹ Although Pt sputtering is costly, this approach is commonly used to fabricate DSSCs on plastic substrates, since they degrade during high-temperature Pt deposition techniques.⁴² A summary schematic of this protocol is shown in Figure S1.

Solar Cell Assembly. The ${\rm TiO}_2$ photoelectrode layer (total thickness 13–14 μ m) was prepared by screen-printing onto an FTOcoated glass substrate. This comprised two layers of transparent TiO₂ paste (18NR-T, Dyesol, Queanbeyan, Australia) and one layer of reflector paste (18RT-AO, Dyesol). After printing the TiO₂ layers, they were sintered at 450 °C for 30 min. The dye was adsorbed onto the TiO_2 by immersing the photoelectrode in dye solution (0.3 mM cis-bis(isothiocyanoto)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-dinonyl-2'-bipyridyl)ruthenium(II), Z907, Dyesol, 1:1 acetonitrile/tertbutyl alcohol solvent) for 24 h. Liquid electrolyte (2 µL, HSE-EL, Dyesol, 3-MPN solvent) was drop-cast on the counter electrode containing the aerogel, forming a gel polymer electrolyte. The cell was sealed with a resin spacer (25 μ m thickness, Surlyn 1702, DuPont, Wilmington, DE) melted at 110 °C. Copper tape was used as external contacts for measurements. Silver paint (Ted Pella Inc., Redding, CA) was applied over the copper-ITO contact to improve conductivity. Finally, epoxy was placed over the silver paint as well as the external perimeter of contact between the glass substrates. A schematic of the aerogel-containing DSSCs is shown in Figure S2. Control/reference liquid electrolyte DSSCs were prepared as described above, except counter electrodes with electrolyte-filling holes were used. After the electrolyte was injected, the holes were sealed by using Surlyn foil.

Electrical Measurements. I-V measurements were obtained by using a Keithley 2450 source meter (Cleveland, OH). Assembled DSSCs were illuminated with a LED lamp (Airam, 4711496, Finland) which was calibrated to give a corresponding amount of illumination to 1 sun in the visible light region. EIS measurements (Gamry Instruments, Warminister, PA) were conducted under 1 sun illumination at open-circuit voltage using a frequency range of 0.1 Hz–100 kHz with a 10 mV ac amplitude. The equivalent circuit model used was similar to those shown in the literature,⁴³ and fitting was done with ZView2 (Scribner Associates, Inc., Southern Pines, NC). To assess reproducibility, 3–4 DSSCs for each test condition were fabricated (N indicated in Table 1), and the result and error reported in Figure 3 and Table 1 represent the average and standard deviation, respectively.

Long-term aging was performed by using halogen lamps (Philips 13117) providing 1 sun intensity in the visible region and 0.2 sun in the UV region. The cells were protected with a UV filter with a cutoff wavelength of 400 nm (Asmetec GmbH). I-V curves were recorded during aging by using an Agilent 34980A multifunction switch measurement unit (Santa Clara, CA) and a BioLogic SP-150

Table 1. Average Resistances and Standard Deviations
Deduced by EIS Measurements Conducted under AM 1.5G
Illumination

sample	no. of cells	$R_{\rm S}(\Omega)$	$R_{\rm CE}\left(\Omega\right)$	$Z_{ m D}\left(\Omega ight)$
85 μm CNC– POEGMA	4	9.7 ± 0.6	6 ± 2	3 ± 1
7 μm CNC– POEGMA	3	11.1 ± 0.8	8 ± 3	3.6 ± 0.2
control	3	9.8 ± 0.6	4.8 ± 0.6	2.5 ± 0.9

potentiostat (Seyssinet-Pariset, France). During the aging, DSSCs were kept at open circuit voltage, and their I-V curves were measured repeatedly from -0.3 to 0.9 V.

SEM Imaging of Aerogel Film. The surface morphology of the CNC–POEGMA aerogel film was observed with SEM (JEOL JSM-7000F, Tokyo, Japan)by using a working distance between 6 and 8 mm and an acceleration voltage of 2 kV. Prior to imaging, the aerogels were coated with 5 nm Pt, and nickel paint (Ted Pella Inc.) was applied to the sample edges to establish conductivity with the metal stub.

Characterization of Bulk Aerogel in Solvent. Aerogel "pucks" were created by using a 17×60 mm glass shell vial (Fisher Scientific, Mississauga, Canada) as a mold. The degradation of aerogel in 3-MPN, ACN, or water was assessed by measuring its relative change in mass over time. The aerogel was immersed in solvent, and its mass was measured after wicking with a KimWipe to remove nonabsorbed fluid. The mass measured over time (M_n) was normalized by M_n/M_s , where M_5 is the aerogel mass after 5 min of immersion. Swelling was assessed by measuring the relative change in diameter of the aerogel puck over time. Top-down photographs of the aerogels were taken with a scale in the field of view. The diameter length was then quantified in ImageJ 1.48v. The diameter length (L_n) was normalized by $L_{\rm p}/L_0$, where L_0 is the length of the dry aerogel. The absorption capability of the aerogel was calculated by using the absorption ratio $(M_5 - M_0)/M_0$, where M_0 is the mass of the dry aerogel. The results presented are the average and standard deviation from at least three aerogel samples.

RESULTS AND DISCUSSION

Aerogel Films as Electrolyte Absorbers in DSSCs. CNC-POEGMA aerogels (1 wt % sol-gel concentration, 1:1 CNC:POEGMA weight ratio) were cast on DSSC counter electrode substrates and patterned into $5 \times 8 \text{ mm}^2$ shapes (corresponding to dimensions of the photoelectrode) by using a stencil lift-off approach as described in previous work (see Figure S1 for schematic of protocol).⁴⁰ This aerogel composition and density were chosen due to its high porosity (>99%, Figure 1),44 solvent stability (Figure 2A), minimal swelling (Figure 2B), high capacity for liquid uptake (Figure 2C), and flexible shape-recovery mechanical properties.⁴⁴ Aerogels at two thicknesses were fabricated by using a 7 or 85 μ m thick patterning mold, resulting in aerogel thicknesses of 10 \pm 4 and 44 \pm 4 μ m, respectively. Liquid electrolyte was rapidly absorbed and retained by the aerogel after drop-casting, allowing for the preparation of the DSSCs without the postelectrolyte filling step. Because of the high porosity of the aerogel scaffold, the liquid electrolyte within the scaffold can wet the nanoporous TiO₂ photoelectrode in a similar manner with the reference (conventional) cells. It should be noted that the thicker aerogel was compressed when assembling the cell, as the FTO-glass was kept apart using a 25 μ m thick spacer. A schematic of the assembled DSSCs is shown in Figure S2.



Figure 1. Representative SEM images of 10 μ m thick CNC–POEGMA aerogel films.

The performance of aerogel-containing DSSCs was compared to conventional liquid-electrolyte DSSCs by using I-V and EIS characterization, the results of which are displayed in Figure 3 and Table 1, respectively. Overall, the standard photovoltaic performance characteristics are similar in all cells. In other words, the minor changes in open-circuit voltage (V_{OC}) and short-circuit current density (I_{SC}) counterbalance each other. These changes relate likely to shifts in the TiO₂ conduction band which are due to the electrolyte filtering effect. The filtering effect causes changes in the spatial distribution of voltage-increasing agents such as 4-tBP or NMBI. A lower amount of these substances results in a decrease in the conduction band leading to a lower V_{OC} , but at the same time more photons can be collected, resulting in an increase of I_{SC} . The uneven spatial performance causes significant losses in larger sized devices, but some effects can occur even at a smaller scale.³¹ In our case, the 44 μ m thick aerogel devices demonstrated small shifts in the $I_{\rm SC}$ and $V_{\rm OC}$, resulting in a slight increase in overall efficiency (η) , which is ascribed to a more even distribution of electrolyte components at the photoelectrode. At a thickness of 10 μ m, the CNC-POEGMA aerogel resulted in no performance differences compared to the control, which is apparent when accounting for the error bar range. The thinner aerogel is barely enough to fill the space between the electrodes, and as such there may be more lateral flow of electrolyte in the cell assembly compared to the thicker aerogel.

The small variations in the fill factor (FF) were investigated with electrochemical impedance spectroscopy (EIS), which identifies individual resistances (see Figure 4 for a representative example). Series resistance accounts for sheet resistance (R_S) , charge-transfer resistance at the counter electrode/electrolyte interface (R_{CE}) , and diffusion resistance $(Z_{\rm D})$ in the cell. $R_{\rm S}$ corresponds to the quality of the transparent conducting oxide layer, which was unaffected during the aerogel casting procedure. It should be noted that $R_{\rm S}$ is highly sensitive to the exact placement of the external current collector contacts, and therefore any variation in that is likely due to small differences caused by handmade preparation of the contacts. R_{CE} relates to the quality of the Pt layer and its ability to catalyze electrolyte redox. It is unlikely that the aerogel significantly hindered charge transfer at the counter electrode/electrolyte interface by blocking the Pt catalyst, as all the aerogel-containing data sets had a high FF. Indeed, EIS confirms that differences in $R_{\rm CE}$ between sample sets are small. Variances that are observed are more likely attributed to differences in Pt film quality between sputtering batches.

Nevertheless, the presence of the aerogel could impede electrolyte diffusion by reducing the volume of free electrolyte and creating tortuosity as well as through steric hindrance from the fibrous network, which could contribute to an increase in diffusion resistance. Indeed, the cells containing aerogels as electrolyte absorbers show a slightly higher average Z_D compared to the control samples, but the difference is not



Figure 2. Characterization of CNC–POEGMA aerogels in various solvents: (A) long-term stability, (B) swelling characteristics, and (C) solvent absorption. Error bars represent the standard deviation of $n \ge 3$.



Figure 3. I-V performance characteristics of DSSCs determined under 1 sun illumination. Error bars represent the standard deviation of $n \ge 3$.



Figure 4. Sample EIS spectra of DSSCs with measured data shown as symbols and fitted results shown as solid lines. Thicker aerogels (44 μ m) are shown in red, thinner aerogels (10 μ m) are gray, and the control liquid electrolyte is shown in black.

statistically significant. One would expect an amplified effect with thicker aerogels, as a great number of diffusive paths and confined regions in the network exist. However, it is interesting to note how the 44 μ m CNC-POEGMA aerogel sample did not give higher Z_D compared to the 10 μ m. It should be noted that the aerogel membranes are highly porous, so even at the larger thickness where the aerogel is highly compressed (~40% compressive strain) down to the volume dictated by the Surlyn spacer (25 μ m thickness), the porosity does not actually decrease much, leaving ample room for charge transfer. Thus, even though the aerogel compression does increase its density, the effects are too small to cause significant impedance to diffusion. This is unique compared to most gel polymer electrolytes reported in the literature where the ionic conductivity and interfacial properties are affected, and thus inorganic nanoparticles are sometimes added to the polymer matrix to restore DSSC efficiency.^{27,45,46} As compared to the earlier work of Miettunen et al.,³⁰ the aerogel fabrication method here allows easier tuning of the aerogel density, porosity, degree of cross-linking (and thus the viscosity of the initial gel and its processability), and thickness control. Furthermore, the freezing conditions used here are milder $(-30 \ ^{\circ}C \ freezing in the freezer vs flash-freezing in liquid$ nitrogen), making the current method more appealing to larger scale fabrication and applicable to more delicate conductive substrates.

An advantage of the CNC–POEGMA composite is its flexibility and mechanical robustness, as it readily demonstrates elastic shape recovery upon compression.⁴⁴ As such, it appears promising for incorporation into flexible DSSCs. To test the feasibility of this approach, the aerogel casting procedure was performed on a flexible ITO-PET substrate (sheet resistance 60 ohm/sq) coated with 20 nm of Pt, which was subsequently used to construct a DSSC. The DSSC with a flexible counter electrode and CNC-POEGMA aerogel, as illustrated in Figure 5, gave similar overall efficiency to those devices with the glass-



Figure 5. Demonstration of (A) dry aerogel and (B) aerogel wetted with electrolyte prepared on flexible ITO–PET substrate (nonplatinized).

Table 2. Performance Parameters of DSSCs with CounterElectrode Prepared on Flexible ITO-PET Substrate

$V_{\rm OC}~({\rm mV})$	695	$R_{\rm S}(\Omega)$	16.4
$J_{\rm SC}~({\rm mA/cm^2})$	13.6	$R_{\rm CE}(\Omega)$	18.6
FF (%)	53	$Z_{ m D} \left(\Omega ight)$	2.9
efficiency (%)	4.98		

based counter electrode (Table 2). The greater R_S value seen in the EIS testing relates to the 4 times higher sheet resistance of the ITO–PET film compared to the FTO glass. Z_D is similar in both glass-based devices and those using ITO–PET, which is to be expected since the substrate should not play a role in electrolyte diffusion within the cell. Interestingly, R_{CE} is higher with the ITO–PET device, which was attributed to the interaction of the Pt layer with PET substrates, where factors such as the different surface roughness vs FTO glass could cause changes in the catalytic performance. Contributions from



Figure 6. Long-term stability measurements of complete DSSCs aged under 1 sun (100% in visible region, 20% in UV region) at 40 °C for 1000 h. Changes in key performance parameters were recorded: (A) $J_{SC'}$ (B) $V_{OC'}$ (C) FF, and (D) η .

the increased resistances account for the relatively low FF. However, the dry and wetted aerogels retained their shape upon bending as shown in Figure 5 and therefore are promising candidate materials for roll-to-roll fabrication, where devices are subjected to significant bending strain.

CNC-POEGMA aerogels can potentially be used as scaffolds to graft performance-enhancing compounds, as both CNC and POEGMA contain chemically versatile hydroxyl groups. For instance, it is understood that doping the electrolyte with graphene nanoribbons can reduce optical absorption from I^-/I_3^- , which has significant effects on cell efficiency in practical applications.⁴⁷ Thus, to assess the suitability of the aerogel for such applications, the long-term chemical and mechanical stability of the aerogel was determined. Aerogel stability was tested by using bulk CNC-POEGMA samples swollen in the common electrolyte solvents ACN and 3-MPN. Water was used as a baseline for comparison. Figure 2A shows that the aerogels were very stable in ACN and 3-MPN, with no significant degradation over a period of ~ 8 months, while aerogels swollen in water progressively degraded after prolonged storage. This behavior is expected, as aerogel stability is dictated by the cross-linking from hydrazone bonds, which are hydrolytically cleavable. On the other hand, the hydrazone bonds are chemically stable in organic solvents that lack nucleophilic species. Therefore, hydrazone cross-linked aerogels are promising as liquid electrolyte absorbents and/or scaffolds for compounds devoid of nucleophilic species.

To ensure that the aerogel does not react with other components in the cell, DSSCs with and without CNC–POEGMA were aged and continuously measured for 1000 h under 1 sun (visible light 100%, UV 20%) at 40 °C. The CNC–POEGMA cells could achieve similar stability results as the control solar cells (Figure 6). It is quite typical that the photocurrent and voltage balance during the first few days. These aging results indicate that CNC–POEGMA aerogels have the potential to be used to absorb electrolyte and are also are structurally stable to be utilized as a scaffold for other functionalities.

CONCLUSIONS

In this work, we demonstrate the use of covalently linked CNC-POEGMA aerogel films as electrolyte absorbing "sponges" for the fabrication of DSSCs. Compared to previously reported methods, the current approach allows easy control of the aerogel density, composition, and final aerogel thickness. Furthermore, we show that due to the hydrazone cross-linking chemistry, these aerogels are very stable in ACN and 3-MPN, the two most commonly used solvents for DSSC electrolyte systems. The DSSC devices prepared from 10 and 44 μ m thick aerogels yielded similar performance and stability as compared to nonaerogelcontaining DSSCs, thus indicating that the used aerogel sponges do not interfere with the electrochemistry inside the device while also improving the ease of the DSSC device fabrication. This fabrication method can also be directly applied to flexible ITO-PET substrate, thus facilitating the production and upscaling of the device size for both glassbased and flexible DSSCs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.9b00795.

Schematics showing the aerogel casting protocol and solar cell assembly (Figures S1 and S2) (PDF)

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Notes

The authors declare no competing financial interest.

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