Spray-Cast Electrodes in Colloidal Quantum Dot Solar Cells for Portable Solar Energy Manufacturing

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***Abstract* — Colloidal quantum dots are a promising candidate material for thin film solar cells due to their size-dependent band gap tunability and solution-based processing flexibility. Spray-casting technology has the potential to reduce the strict environmental requirements associated with traditional fabrication procedures for colloidal quantum dot solar cells, potentially enabling installation-site solar cell fabrication. Here, we demonstrate spray-casting of silver nanowire electrodes and zinc oxide electron transport layers, demonstrate their use in colloidal quantum dot solar cells, analyze the existing challenges in current spray-casting procedures, and outline a path to producing fully spray-cast colloidal quantum dot solar cells.**

***Index Terms* — colloidal quantum dots, silver nanowires, spray-casting, thin film solar cell, Zinc Oxide.**

I. Introduction

Colloidal quantum dots (CQDs) are a promising candidate material for thin film solar cells due to their size-dependent band gap tunability and solution-based processing flexibility [1]. This flexibility in theory should allow colloidal quantum dot solar cells to be coated on any surface such as the sides of buildings, on windows, and in remote locations. Even though the costs of traditional silicon solar cells have been continuing to decline, their applications are still limited because of the rigid and heavy nature of their modules. This limitation could potentially be broken by flexible colloidal quantum dot solar cells [2]. However, there are several factors limiting the scalable and deployable fabrication of colloidal quantum dot solar cells. The current best-performing cells [3] are formed using high-temperature-processed transparent conductive oxides (TCOs), non-portable and non-scalable spin-casting processes to deposit the colloidal quantum dot and charge transport layers, and time-consuming physical evaporation of the top and bottom electrodes which requires low pressures. These lab-level methods limit the scalable fabrication of colloidal quantum dot solar cells.

Our ultimate goal is to build a fully spray-cast flexible colloidal quantum dot solar cell, in which all cell layers, including the electrodes, are deposited using an inexpensive and deployable manufacturing method. Spray-casting has several advantages for thin film solar cell manufacturing. First, the spray-casting process has a 100% utilization rate of the starting ink material compared with traditional spin-casting processes which waste a large fraction of the starting ink, saving on materials costs [4]. Second, the spray-casting process can be applied onto virtually any surface, which makes it possible to fabricate colloidal quantum dot solar cells on flexible substrates, on wearable device skins, automobile surfaces, or directly onto urban infrastructures [5]-[6]. Third, by replacing the evaporated gold contact with a low-temperature spray-cast silver nanowire contact, the low-pressure requirement can be removed from the fabrication procedure, making it possible to fabricate solar cells on-site in any environment, which reduces the potential costs.

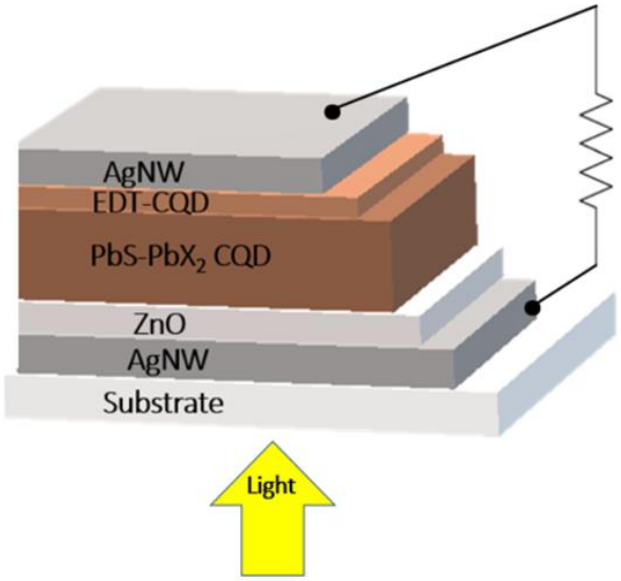

Fig. 1. Schematic of a fully spray-cast colloidal quantum dot solar cell structure on a flexible substrate. AgNW refers to the silver nanowire-based transparent electrode. EDT-CQD refers to the ethanedithiol-treated hole-collecting PbS CQD layer. PbS-PbX_2 CQD refers to the PbI_2/$PbBr_2$-treated light-absorbing PbS CQD layer. ZnO refers to the zinc oxide electron transport layer.

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A schematic of the full layer structure of a flexible colloidal quantum dot solar cell is shown in Figure 1. The silver nanowire layer and the zinc oxide layer are spray-cast onto a transparent substrate (glass, transparent plastic, or similar). PbS colloidal quantum dots capped with oleic acid ligands in octane are synthesized by modifying previously published methods [7]. A solution-phase ligand exchange is performed using PbI_2, $PbBr_2$ and ammonium acetate in dimethylformamide (DMF) to get $[PbX_3]^-/[PbX]^+$-capped PbS colloidal quantum dots, and the colloidal quantum dots are dispersed in a mixture of butylamine and DMF for spray-casting the $[PbX_3]^-/[PbX]^+$-capped PbS colloidal quantum dot absorbing layer. A thin layer of oleic acid-capped PbS colloidal quantum dots is sprayed on top of the absorbing layer, followed by spraying of 1,2-Ethanedithiol (EDT) in acetonitrile to perform a solid-state ligand exchange. This is followed by a pure acetonitrile spray step to wash the film and remove the oleic acid ligands, forming the EDT-capped PbS colloidal quantum dot hole transport layer [8]. In this work, we are focusing on the demonstration and optimization of the spray-casting processes for the bottom transparent electrode layer (silver nanowires) and the electron transport layer (zinc oxide).

II. Experimental Methods, Results And Discussion

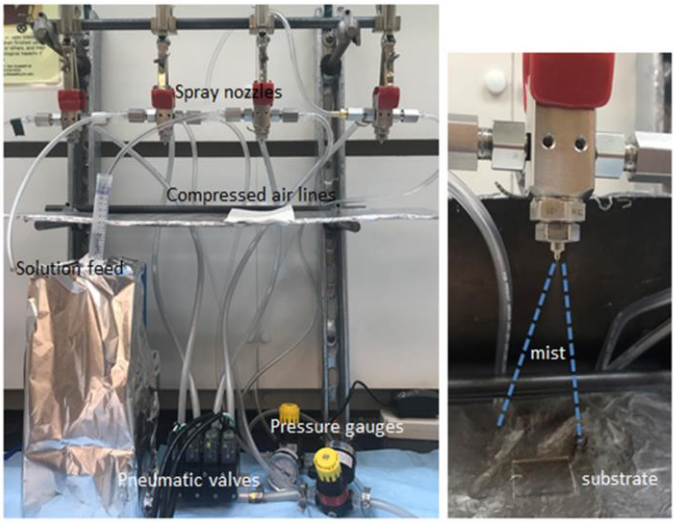

Fig. 2. Left: The spray-casting system. When compressed air is supplied through the air lines, the siphon effect pushes the solution from the feed into the nozzles, and the spray-casting process commences. The pilot air is switched by the pneumatic valves, and the air pressure is controlled by the pressure gauges. Right: A magnified image of one spray-casting nozzle in action. A fine mist of the target material is applied to the substrate.

Our work is based on the custom-built automated spray-casting system shown in Figure 2. The liquid-siphon-fed fine fog nozzle is controlled by a pneumatic valve, whose on/off function is switched by an external electrical power controller. Setting the controller to "on" provides pilot air to the nozzle. When air is supplied to the system, the siphon effect pushes the solution into the nozzle, and the spray-casting process commences. By adjusting the air supply pressure, the pilot air pressure, the distance between the nozzle and the substrate, the total spray duration, and the spray pattern (continuous spray or alternating spray/pause cycles), we are able to modify the droplet size of the mist, as well as the thickness and quality of the spray-cast thin film.

A. Silver nanowire layer optimization

Silver nanowires are a promising candidate material for transparent electrodes in flexible thin film solar cells due to their solution processability and flexibility. Additionally, spray-casting of silver nanowires can be done at ambient conditions. The two most important parameters for transparent electrodes are conductivity and transparency, which are typically anti-correlated; optimizing both simultaneously requires a trade-off. The conductivity of spray-cast silver nanowire electrodes is generally determined by the degree of interconnection between individual silver nanowires forming the nanowire network. Longer silver nanowires generally lead to better conductivity [9]-[11]. In this work, we use a commercial silver nanowire solution (Sigma-Aldrich, 5 mg/mL, 70 nm (±10 nm) diameter, 40 μm (±5 μm) length, dissolved in isopropanol) as our source. Experiments show that diluting the solution to 0.5 mg/mL leads to the best spray-cast films and provides the optimal balance between being too viscous to create a continuous solution feed and too sparse to produce a uniform thin film.

The sheet resistance of the transparent electrode is measured using our home-built four-point-probe system, and the transmittance is measured using a Cary5000 UV-VIS-NIR spectrophotometer. Table 1 is a summary of our silver nanowire spray-casting parameter optimization trials and results. A discontinuous spray pattern (1-minute-spray, 1-minute-dry cycle) gives the best trade-off between conductivity and transparency. This spray pattern allows enough time for the solvent to dry before forming big droplets, while the drying time is not too long for the nanowires to build strong adhesion to the substrate and form interconnected networks. The transmission curves, which include measurements of conventionally-deposited indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) control films, show that the best-performing spray-cast silver nanowire electrode provides transparency comparable to that of the control TCOs in the visible range and significantly better transparency in the near-infrared range while maintaining an acceptable conductivity (Figure 3). This property is crucial for PbS colloidal quantum dot solar cells because one major advantage of this photovoltaic platform is its infrared solar energy harvesting ability [12]-[13].

Trial	Nozzle-Sample Distance (cm)	Spray Time (min)	Dry Time (min)	Spray Cycles (#)	Transparency (avg % across 400-2000 nm)	Sheet Resistance (Ω/square)
1	5	5	15	1	50	18
2	8	6.5	30	6	86	29
3	8	4	15	1	75	474
4	6	3	15	1	80	693

Table 1. Spray-casting parameters and optimization results for silver nanowire electrodes.

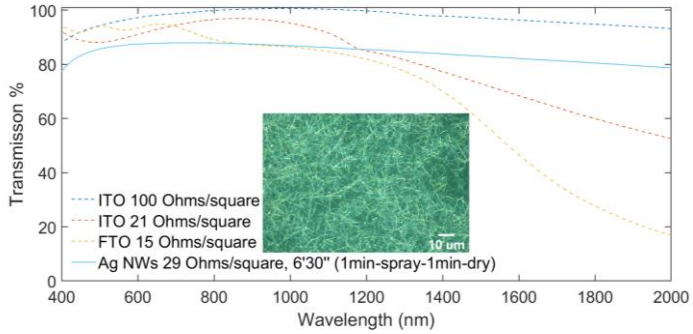

Fig. 3. Transmission curves for the best-performing spray-cast silver nanowire electrode and transparent conductive oxide control samples. The 100 Ohms/square ITO and the 21 Ohms/square ITO have thicknesses of 70 nm and 350 nm, respectively. Inset: An optical microscope image of the silver nanowire film.

B. ZnO layer optimization

Zinc oxide (ZnO) is widely used as the electron transport layer in several types of solution-processed solar cells [14]-[15]. We synthesize ZnO nanoparticles using zinc acetate dihydrate, methanol and KOH as the precursors, purify the particles by adding toluene and hexane and centrifuging, and dissolve the final particles in methanol [16]-[17]. We optimize the spray-cast ZnO layer by modifying the solution concentration and the spray pattern. We identified 2 mg/mL as the optimum concentration for our current spray-casting process. We spray-cast ZnO on ITO- and FTO-coated substrates, as well as on the spray-cast silver nanowire substrates. The spray-cast ZnO-on-ITO (10 minutes continuous spray) resulted in a thin film with a mean thickness of approximately 100 nm (measured using a Keyence VK-X 3D Laser Scanning Confocal Microscope), which is similar to the thickness of our conventional spin-cast ZnO layer. We have also fabricated a complete working solar cell device based on a spray-cast ZnO thin film layer on an ITO substrate. The current density-voltage curve for the device is shown in Figure 4. The preliminary device had an open circuit voltage of 0.54 V, a short circuit current density of 18.8 mA/cm^2, a fill factor of 0.53, and a power conversion efficiency of 5.4%. This device served as a proof-of-principle demonstration of the feasibility of using spray-cast electrode layers in thin film solar cells, and device performance will be optimized in future work.

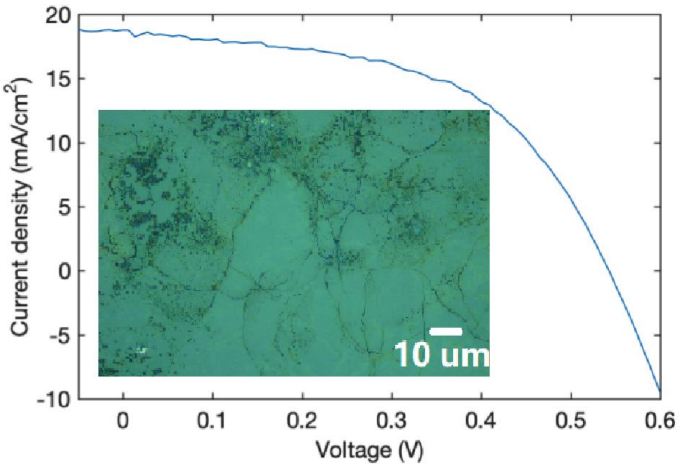

Fig. 4. Current density-voltage curve under simulated solar illumination for a CQD solar cell device based on a spray-cast ZnO layer on an ITO-coated substrate. (Inset) An optical microscope image of the spray-cast ZnO film.

C. Discussion

Our spray-cast silver nanowire electrode has a good trade-off between conductivity and transparency. However, its performance in full devices is currently limited by its surface roughness, which is known from the surface topography measured under laser scanning microscope, since the roughness makes it difficult to form a continuous ZnO electron transport layer which leads to short-circuiting of the entire device. This roughness is caused by the random directions in which the silver nanowires align on the substrate during deposition, with many oriented vertically as opposed to horizontally across the plane of the substrate. Future work will involve strategies to reduce the surface roughness including optimizing the spray-casting parameters to produce more continuous films and adding thermal and chemical annealing steps to improve smoothness.

We have shown that a spray-cast ZnO layer can serve as the electron transport layer in a working solar cell device. However, the figures of merit leave room for improvement due to deficiencies in the coverage and smoothness of the layer. In future work, we will optimize the spray-cast ZnO layer in order to reduce the surface roughness and promote better adhesion between the silver nanowire film and ZnO. The next step is to develop a spray-casting process for the colloidal quantum dot layers and demonstrate a fully spray-cast colloidal quantum dot solar cell device.

III. Summary And Future Work

In conclusion, we have successfully built a semi-automated spray-casting system capable of depositing different

optoelectronically-relevant inks and have produced a spray-cast silver nanowire electrode with a conductivity-transparency trade-off that is comparable to the best oxide-based transparent conducting electrodes with improved near-infrared transparency. We have also demonstrated a colloidal quantum dot solar cell device with a spray-cast ZnO electron transport layer. This proof-of-principle demonstration should enable flexible deployment of solar energy harvesting technologies on a variety of urban infrastructures and surfaces in remote locations. Future work will focus on further improving the quality of the spray-cast ZnO and silver nanowire films with the goal of reducing surface roughness and improving device performance. We are currently using strategies such as encapsulating the silver nanowire layer in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), heating the substrates during spray-casting, and using mechanical pressure to realign the vertically-oriented silver nanowires after deposition to enable better coverage of the ZnO onto and into the silver nanowire network and reduce the surface roughness issues associated with the silver nanowire electrode. Additionally, we are optimizing the ligand exchange processes for the PbS colloidal quantum dot layers and developing a spray-casting process for them. We plan to demonstrate the spray-casting processes on flexible substrates such as polyethylene terephthalate (PET) films. Finally, we will build a fully spray-cast colloidal quantum dot solar cell, scale up the spray-casting processes and apply them to other solution-processed optoelectronic technologies.

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