

Efficient Spray-Coated Colloidal Quantum Dot Solar Cells

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Solution-processed semiconductors offer the promise of low-cost, production-scale optoelectronic devices such as solar cells. Unfortunately, most reports are limited to lab-scale, batch-processing methods such as spin coating and dip coating. Strict requirements on their nano- and microscale morphology account for the sub-par performance of spray-coated bulk heterojunction organic and polycrystalline inorganic solar cells. Here, we report record-efficiency spray-coated solar cells that employ an active layer that is deposited under ambient conditions and whose composition was selected to overcome the morphological constraints characteristic of other solution-processed technologies. Hypothesizing that planar solar cells based on predefined nanoparticles would provide a better platform for spray coating, we explored the use of colloidal quantum dots as the active material. Only by developing a room temperature spray-coating technique and implementing a fully automated process with near monolayer control, an approach we termed as sprayLD, a solar cell performance and statistical distribution are achieved that are superior to prior batch-processed methods along with hero performance of 8.1%.

Scale-up manufacturing methods, in contrast with batch-level spin coating onto discrete substrates,^[1–3] seek to coat large substrate areas using a continuous roll-to-roll process. Spray

coating (Figure 1a) has been used to deposit the active layer of photovoltaic devices based on organic materials^[4–8] and ternary nanocrystals;^[9] however, the power conversion efficiency (η) of such devices has remained well below the performance of their batch-processed counterparts. This reduction in performance upon scale-up is attributable to the failure of spray coating to implement the nano- and microscale morphologies of organic (the interpenetrating nanoscale bulk heterojunction) and inorganic (well-passivated microscale polycrystalline) solar cells (Figure 1b, top and middle).^[8–11]

We turned our attention instead to colloidal quantum dots (CQDs), solution-processed semiconductors that have risen rapidly in performance in recent years as solar light harvesters.^[12] CQDs can in principle exceed the single-junction Shockley–Queisser solar efficiency limit^[13] through multijunction architectures^[14,15] and multiple exciton generation.^[16,17] Since these materials are stored in and deposited from solution, they are well suited to large-scale, low-cost manufacturing processes. One recent report showed that a CQD-based ink is able to (with the aid of thermal annealing) produce a solar cell exhibiting just over 1% power conversion efficiency.^[18] Spray-deposited nanocrystals formed via in-flight crystallization/precipitation,^[19,20] or through a high temperature spray pyrolysis,^[21] have shown initial promise from a materials composition perspective, whereas mist deposition of CQDs has been used in light emission applications.^[22]

The promise of CQDs for spray-coated photovoltaics resides in significant part in the fact that, following their synthesis, the materials are already fully formed—well-defined as nanocrystals—to serve as solution-phase precursors to CQD films. This notably simplifies the degree of morphological and chemical control required in the ensuing coating process (Figure 1b, bottom).

We developed a fully automated spray coater for CQD solar cell fabrication (Figure 2a; Figure S1-1, Videos S-V1 and V2, Supporting Information). A fine mist containing oleic acid capped CQDs dispersed in octane was atomized using pressurized nitrogen gas and deposited on a transparent conductive oxide/TiO₂ stack as described previously.^[3,23] Layers were treated using 3-mercaptopropionic acid (MPA) in methanol to exchange the long aliphatic oleic acid ligand with the shorter MPA molecule, and then rinsed with methanol. An air blade was used to apply a curtain of high pressure compressed dry air to aid in solvent drying. This process is repeated a number of times to achieve the final desired thickness (see Experimental Section). This setup is fully computer controlled to make fabrication consistent across multiple layers and multiple devices.

We first explored whether direct translation of existing spin-coating methods could produce devices having efficiency

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