Challenges in Quantum Dot Solar Cells: To aid or prevent oxygen doping?

Cathy Chang

July 21, 2021

email: *cathy.chang.ct@gmail.com*

ABSTRACT: In colloidal quantum dot solar cells (CQDSC), quantum dots between the size of 2nm to 10nm are suspended in colloidal quantum dot (CQD) fluids and distributed on the solar cell to form p-type or n-type semiconducting layers. However, oxygen in the ambient air may stabilize or corrode the CQDSC depending on the type of semiconductor layer that is exposed to ambient air. In this paper, I will review two approaches in the manufacturing of top-facing layers of quantum dot solar cells. The first approach aims to aid oxygen doping for p-type CQD, thereby promoting long-term cell performance stability. The second approach aims to prevent oxygen corrosion for n-type CQD by passivating the surface, enabling future research to use n-type CQD as top-facing layers. These strategies address key performance stability and manufacturability challenges in CQDSC development.

1. INTRODUCTION

1.1. Background on solar cells

Across the United States, seas of silicon solar panels have cropped up as an alternative to fossil fuels in response to increasing awareness on climate change. The alarming effects of climate change, including polar ice melting, groundwater contamination, and species extinction, have caused our society to utilize electricity as a replacement energy source.

A driver of this transformation are solar cells, or photovoltaics, a means of generating electricity from sunlight (1). Photovoltaics employ layers of semiconductors to transduce photons from the sun to electricity through the photoelectric effect.

While silicon has dominated the commercial market for semiconducting layers for solar cells, concerns over its efficiency and environmental impact in manufacturing process have ignited research in alternative materials. One of the leading contenders are colloidal quantum dot solar cells (CQDSC), which are solar cells using colloidal quantum dots (CQD) the semiconductor layers. Quantum dots are nanoparticles with high bandgap tunability, multiple exciton generation, material abundance, and have an energy-efficient manufacturing process, thus making them attractive candidates for photovoltaic materials.

1.2. Quantum dot promises and challenges

While colloidal quantum dot solar cells (CQDSC) are still in the early stage of development, they already show promise over silicon solar cells as they require significantly less energy to be produced and offer greater flexibility in their electrical properties due to the tunability of quantum dot size. Most importantly, CQDSCs have the potential to surpass the 33% theoretical efficiency limit of traditional cells by producing more energy per photon absorbed. Beyond the photovoltaics field, quantum dots also show promise in light-emitting diodes (LEDs), field-effect transistors, digital displays, and medicine (2).

However, despite theoretical promises in high power conversion efficiency (PCE), quantum dot solar cells remain at around 10% PCE between 2014 and 2016 due to challenges in cell stability and manufacturing scalability. Such challenges arise from variable humidity in manufacturing conditions, cell instability in ambient air, and a currently unoptimized manufacturing processes. Two distinct research approaches have emerged to solve the aforementioned issues: The first group examines p-type CQD as the absorbing layer, and the second group examines n-type CQD as the absorbing layer. A detailed discussion of both devices will be presented in the later section.

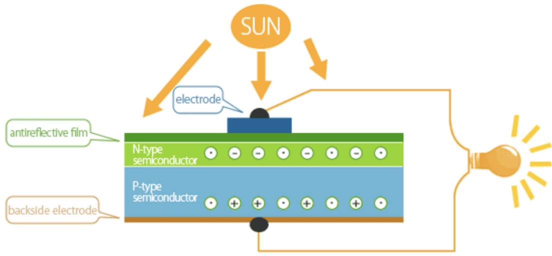

Fig. 1: Figure 1. Structure of a solar cell, with n-type solar cell as the top-facing absorbing layer. A photon hits the n-type semiconductor, resulting in an electron from the n-type semiconductor and hole in the p-type semiconductor. This forms an electron-hole pair (exiton pair), which is then separated by the p-n junction. The flow of this exiton pair generates electricity. (4)

1.3. Challenges and solutions

In solar cell technology, electricity is generated by two types of semiconductor layers working in tandem: the n-type and p-type semiconductors 1. N-type semiconductors have an excess of free electrons, while p-type semiconductors contain 'holes' where electrons can move through. These layers are typically stacked together, and when photons from sunlight strike the solar cell, electrons in the n-type layer gain energy and move to the p-type layer through these holes, creating a flow of electric current. This movement of electrons across these so-called p-n junctions are the fundamental mechanism by which solar cells convert light energy into electrical energy. However, both n-type and p-type semiconductors face unique issues as the outer (absorbing) layer in such devices.

Researchers working with p-type CQD as an absorbing layer face difficulties during the manufacturing process, leading to cell performance instability and wasted materials. During manufacturing, humidity in the air repels oxygen from interacting with p-type CQD, hindeingr oxygen from donating extra electrons to the material through a process called oxygen doping (3). Without the extra electrons from oxygen doping, CQDSC produces significantly less electrical current.

Conversely, researchers using n-type CQD face oxidation challenges once the cells are exposed to oxygen in ambient air, rendering them ineffective for generating current. This limitation prevents research groups from using n-type CQD as the absorbing layer since it cannot interact with ambient air.

2. CURRENT RESEARCH

2.1. P-type Promoting Oxygen Doping

In 2018, Ning et al. found that the lack of oxygen doping due to humidity in ambient air deteriorates cell performance with p-type CQD as the absorption layer (5). While manufacturing the CQDSC under "variable moisture and environmental conditions" (5), they found an absolute humidity of $5\,\mathrm{g\,m^{-3}}$ yielded a PCE of 10%, whereas an absolute humidity of $12\,\mathrm{g\,m^{-3}}$ reduced the PCE to 5%. Such deficiencies were concluded to be due to high humidities yielding suboptimal transportation layer geometry, leading to band alignment issues and subsequently poor efficiency (5).

This is an alarming finding, as most manufacturing plants cannot control their humidity levels with ease, especially in regions with varying climate conditions. In humid cities such as Taiwan and Thuwai, fabrication is bottlenecked by humidity year-round, whereas in seasonally dry cities such as Beijing and San Jose, the fabrication bottleneck is during the summer. Even during these winter months, only 2-3 cities achieve the optimal $< 5\mathrm{g\ m^{-3}}$ absolute humidity mentioned earlier.

The solution Ning et al. came up with was surprisingly simple yet highly effective: store the CQDSC in dry air, approximately $< 5\mathrm{g\ m^{-3}}$ humidity, after manufacturing. The dry air allows oxygen species attach to the quantum dots and create extra hole energy levels that allow holes to easily rise to the valence band. This oxygen doping process permanently restores the PCE from approximately 5% to 10%.

Having overcome the challenge of fabrication in ambient air, the researchers tackled the scalability of CQDSC films under similar conditions. Traditional techniques like spin-coating and spray coating are inefficient and wasteful. In spin-coating, a small amount of CQD is applied at the center of the spinning substrate. Centrifugal force then propels CQD to spread across the substrate. This process is repeated multiple times to get multiple layers because CQD is not concentrated enough to successfully coat everything in one spin. Much of the CQD goes to waste when it spins out of the substrate. In addition to its wastefulness, it also requires multiple applications to completely coat the substrate. Spray coating contains the same material wastage issue; it requires 3x more CQD material than spin-coating.

Therefore, the researchers introduced high-speed blade coating to replace spin-coating and spray coating under ambient conditions. Blade coated devices achieve performance equal to spin-coated devices, while using only 4% of CQD. In blade coating, highly concentrated CQD ink is slathered on the film with a blade in a single sweep. To put things in perspective, the amount of CQD material by mass needed to fabricate a spin-coated solar cell can fabricate 25 blade coated solar cells.

The humidity-resilient fabrication technique enables researchers from all over the globe to manufacture quantum dot solar cells in various seasons, and the blade-coating technique leads to approximately 96% saved CQD material. These advances allow researchers to continue pursuing higher efficiency solar cells without fearing a loss in performance.

2.2. N-Type Preventing Oxygen Doping

In 2014, Kirmani et al. examines a different oxygen doping problem, where the n-type CQD suffers from oxygen doping when exposed to ambient air because oxygen will take away free electrons. Prior to this paper, the solution to this problem is 1) to use p-type CQD as the top layer to prevent oxygen from getting to the n-type CQD and 2) to encapsulate n-type CQD using atomic layer deposition to prevent direct oxygen invasion (4). Their research aims to enable n-type CQD operable in ambient air without encapsulation.

To create un-encapsulated n-type CQD, the researchers adopted a passivation technique with organic ligands that passivate the dangling bonds on the CQD surface, preventing oxygen from binding with the film. They first narrowed their organic ligand choice down to the halides because of their "n-type doping character in CQD solids" (4) and their small hindrance in nanoparticle surface coverage. Then, they determined experimentally that iodide ligands perform the best among iodide, bromide, and chloride ligands because of its larger atomic radius and strong binding force. Combining both characteristics, the strong binding force aids the iodide in binding to the surface through rigorous chemical wash, whereas the larger atomic radius better protects the surface of CQDs compared to smaller halide atoms.

In contrast to untreated CQD, iodide ligands treated with CQD achieve almost no loss in performance or characteristics, whereas untreated CQD sees a near-instant $> 20\%$ performance loss in air exposure 4 days. Moreover, the doping density of the n-type film as well as n-type characters remain stable under air exposure. In short, passivating the n-type CQD film surface with iodide ligands ward off oxygen species attacks in ambient air while retaining its initial performance.

The new passivation technique that wards off oxygen species from oxidizing the n-type CQD films. In the past, most research groups did not use n-type CQD films because they are notoriously prone to oxidation in ambient air. This solution allows for n-type CQDs as absorbing layers and opens up new avenues for new CQDSC variants.

3. CONCLUSION

Although quantum dots have yet to replace silicon in the solar cell field, their journey mirrors that of transistors in electronics, which eventually became the basic building block of our modern world. Similar to the early days of transistor development, where entry to commercial markets first occurred via devices like radios, quantum dots have entered the commercial market via LED TVs. Just as transistors faced manufacturing and scalability challenges during their initial conception, CQDSC are currently navigating similar challenges in manufacturability and stability.

Many research groups have made significant strides towards overcoming these challenges. The first group's approach of storing p-type CQDSC in humidity-controlled environments opens the door for scalable manufacturing that is agnostic of the local climate of a manufacturer. Meanwhile, the techniques introduced by the second group offer potential for utilizing n-type layers as top-facing absorbing layers, paving the way for a new solar cell variant. Just as transistors eventually revolutionized electronics, the ongoing research and development in CQDSC may pave the way for a future where scalable, efficient quantum dot solar cells will introduce an era of sustainable energy production.

REFERENCES

[1] "Advantage of solar cell which is environmentally-friendly," Electronics and Materials Corporation Limited.

[2] M. A. Cotta, "Quantum dots and their applications: What lies ahead?" *ACS Applied Nano Materials*, vol. 3, no. 6, pp. 4920–4924, 2020. [Online]. Available: https://doi.org/10.1021/acsanm.0c01386

[3] R. Nave, "Bands for doped semiconductors," Hyperphysics. [Online]. Available: http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/dsem.html

[4] Z. Ning, O. Voznyy, J. Pan, S. Hoogland, V. Adinolfi, J. Xu, M. Li, A. R. Kirmani, J.-P. Sun, J. Minor, K. W. Kemp, H. Dong, L. Rollny, A. Labelle, G. Carey, B. Sutherland, and I. Hill, "Air-stable n-type colloidal quantum dot solids," *Nature Materials*, vol. 60, no. 7, July 2014.

[5] A. R. Kirmani, A. D. Sheikh, M. R. Niazi, M. A. Haque, M. Liu, F. P. G. de Arquer, J. Xu, B. Sun, O. Voznyy, N. Gasparini, D. Baran, T. Wu, E. H. Sargent, and A. Amassian, "Overcoming the ambient manufacturability-scalability-performance bottleneck in colloidal quantum dot photovoltaics," *Advanced Materials*, 2018.