Current Challenges in the Development of Quantum Dot Sensitized Solar Cells

Iván Mora-Seró

Quantum dot sensitized solar cells (QDSSCs) have experienced a continuous performance growth in the past years presenting a photoconversion efficiency >13%. QDSSCs constitute a smart approach to take advantage of the properties of semiconductor quantum dots (QDs), mitigating the transport constrains. In contrast with other QD solar cell configurations, for QDSSCs, the record efficiencies have been reported with Pb and Cd-free based sensitizers. The development of techniques in order to provide photoanodes with very high QD loading and the discovery of new electrolytes, including all solid configurations, are the most important future challenges that this technology must address to further increase cell performance and stability.

Reducing the semiconductor size to dimensions in the same order or lower than twice the exciton Bohr radius allows tuning the properties of the semiconductor material, being the control of the bandgap the most manifest feature. This is the so-called quantum confinement regime, and the nanocrystals exhibiting it in the three space dimensions are also known as Quantum Dots (QDs). Semiconductor QDs are an easily tunable family of materials with excellent optoelectronic properties. They can be synthesized at relatively low temperature, even at room temperature, in contrast with their bulk counterparts. These properties give QDs an immense potential for the development of optoelectronic devices, including energy applications in photovoltaic devices. However, their application to the fabrication of photovoltaic devices is constrained mostly by carrier transport limitations.

The individuality of the QDs, represented by the nanocrystal surrounded by the capping ligand, confines the exciton in a small regions. This fact presents advantages for the development of light emitting diodes (LEDs). However, this structure hinders the charge transport properties. In the photovoltaic process two consecutive step are required. First, light has to be absorbed creating photogenerated carriers, splitting electron, and hole Fermi levels. However, a second step of charge separation at the selective contacts is necessary in order to convert the free energy harvested in the first step into usable work. In QD solar cells, a light absorbing layer, formed by colloidal QDs as building blocks, is sandwiched between two different electron and hole selective contacts. In order to maximize the photogenerated power, all the incident light has to be absorbed by the QD layer, requiring QD films with at least several hundred nanometer thickness. At the same time, photogenerated electron and holes have to be transported through the QD layer to their respective selective contact, before they recombine. The presence of ligands between QDs, non-passivated trap states, and QD size distribution, causing a bandgap distribution where photogenerated carriers can be trapped in low bandgap QDs, hinders carrier transport in colloidal QDs solar cells, as we discuss below.

An interesting alternative to this configuration is the QD Sensitized Solar Cell (QDSC) structure, similar to the Dye Sensitized Solar Cells (DSSCs) but using semiconductor QDs instead of molecular dyes to sensitize a mesoporous electrode to visible light. In DSSCs, a molecular dye absorbs light and photogenerated electron and hole and quickly injected into two different transporting media. In conventional solar cells electron and holes are transported to the selective contacts through the same media in which both are photogenerated. Consequently, both kind of carriers cohabit in the same material until they are extracted at the selective contacts, increasing the probability of recombination. In contrast, in DSSCs just one kind of carrier is transported by each transporting media. As electron and hole transporting materials (ETM and HTM, respectively) just contain one kind of carrier, and consequently recombination is reduced, it allows to relax the high quality requirement of these materials, generally needed to reduce recombination. In addition, transport is mainly related to the individual properties of these materials rather than to the properties of the QD light.
absorber, permitting to bypass some of the transport limitation of QD thin films. In addition, to ensure the collection of the incident light in QDSSCs, a mesoporous electrode to increase the effective surface area, formed by nanoparticles (commonly of TiO$_2$) with several tenths of nanometers size, are used as ETM. Eventually, the use of a redox couple in a liquid electrolyte guarantee the contact of mesoporous structure acting as HTM.

QDSSCs represent the triumph of an idea since their beginnings were not very promising. First report of the sensitization of nanoporous TiO$_2$ electrodes with colloidal InP QDs showed photoconversion activity even with a very poor performance with external quantum efficiency (EQE) of <1%. Interestingly, 12 years later in 2010, the first experimental demonstration of internal quantum efficiency (IQE) higher than 100%, in fact close to 200%, taking advantage of the multiple exciton generation in PbS QDs, was reported for QDSSC configuration. One year later, the first demonstration of EQE > 100% was reported for thin-film colloidal QD solar cell configuration.

At the early stages of QDSSCs, this technology had to face two main challenges, that in fact although with different nuances they are the same ones that QDSSCs are currently facing: QD loading and device long term stability. At the beginning of this century, DSSC was a scientifically established technology with a standard configuration formed by a mesoporous TiO$_2$ photoanode, the sensitizer dye, a liquid electrolyte using iodine/iodide redox couple, and a platinum counter electrode to regenerate the redox couple extracting holes. In this established structure, the substitution of one part by another, i.e., the molecular dye by the semiconductor QD, does not change the concept but distorted the experimental feasibility. On the one hand, colloidal QDs with long molecular capping present sizes of the same range than the pores of the standard nanostructured electrode used, limiting the QD loading and consequently the light harvesting. On the other hand, most QDs are not stable in iodine/iodide electrolyte, and new redox systems are required. At the same time, the change of redox couple also force the use of an appropriated capping material. In summary, the structure of QDSSCs has to be rethought with respect to DSSCs in order to increase the performance and the stability. For example, it was needed to use a new HTM in comparison with DSSCs, being the most widespread an aqueous electrolyte with polysulfide redox and brass counter electrode suited for this redox system.

The strategy of growing directly the semiconductor QDs on the surface of the porous electrodes allowed to increase the QD loading. Chemical bath deposition (CBD) or successive ionic layer adsorption and reaction (SILAR) permitted the growth of semiconductor QD on the surface of the mesoporous photoanodes. However, the crystal quality of the QDs grown by these methods is lower than the obtained for colloidal QDs and subsequent passivation is needed. ZnS passivation, that reduce the photocarrier recombination, has demonstrated a huge success in order to increase the performance of QDSSCs, not just in the case of QDs grown by CBD or SILAR but also for colloidal QDs. In fact this treatment is a standard step in most of the current QDSSCs, and QD passivation has been one of the most commonly used strategies in order to improve the performance of QDSSCs. The use of QDs directly grown on the mesoporous electrode allowed to increase the photovoltaic conversion efficiency (PCE) to 4–5%.

The easy preparation of QDSSCs by low demanding techniques as CBD and SILAR, where sensitization just require bath or dipping in simple solutions with the precursors, and also the lower cost in comparison with DSSCs (mostly due to the cost of precursors for QDs, redox, or counter electrode), popularized enormously QDSSCs despite at that stage the PCE remained significantly below the PCE reported for DSSCs. Probably QDSSCs are the solar cells more easy and accessible for preparation allowing many research group, even with limited resources, to start a research line on this topic. This fact allowed that many groups incorporated into the QDSSCs research pushing the interest and results of this field.

However, the crystalline quality of QDs directly grown on the mesoporous electrode was limiting the QDSSC performance. QDSSCs prepared with colloidal QDs presented just slight lower performance than the ones prepared with QDs directly grown, despite the former presented much lower light absorption than the later, indicating the superior potentiality of colloidal QDs for the development of solar cell and the limitation arisen from the QD loading. Different techniques were investigated to sensitize mesoporous electrodes with colloidal QDs as direct absorption of as synthesized QDs or the use molecular likers to anchor the colloidal QDs to the photoanode surface. Zhong and co-workers developed a capping-ligand-induced self-assembly (CLIS) method to increase the colloidal QD loading in sensitized electrodes, by pipetting the mercaptopropionic acid (MPA)-capped core/shell CdS/CdSe colloidal QD aqueous solution onto the TiO$_2$. The increase of colloidal QD loading boosted for the first time the performance of colloidal QDSSCs beyond 5%, but most importantly focuses the attention on colloidal QDs as sensitizer and all the subsequent performance records in QDSSCs have been obtained with colloidal QDs.

Currently the performance of QDSSCs has surpassed 13% in the same range than DSSCs, and the fight to increase the QD loading is still at the center of the development. Different groups have achieved an efficiency >13%. Zhong and co-workers reported the highest QDSSCs laboratory and certified efficiencies, 13.71% and 13.49%, respectively, taking advantage of a proper passivation of core/shell colloidal QDs. Moreover, efficiencies >13% have been also obtained by increasing the QD loading with two consecutive QD deposition. The deposition of a surfactant after the colloidal QD sensitization allowed a secondary deposition of QDs, see Figure 1a, while a second deposition is also possible by sequential immersion in aqueous solution with the colloidal QDs, see Figure 1b. The co-sensitization has been also used in DSSCs and in QDSSCs to extend the light harvesting range. Interestingly, also hybrid co-sensitization using QDs and dyes designed to link to the QDs have been developed. However, beyond the broadening of the light absorption range, a second cycle of deposition, even with the same QD type, can improve loading and cell performance.

The current PCE records for QDSSCs has been obtained with Zn-Cu-In-Se (ZCIS) and/or Zn-Cu-In-S (ZCIS) QDs. Despite, most of the first reports on QDSSCs were based on Pb or Cd containing materials as CdS, CdSe, or PbS, in contrast with other semiconductor solution processed photovoltaics, high performances have been attained with Pb and Cd-free materials, as CuInS$_2$, ZCIS, or ZCISe. While thin-film colloidal QDs have been developed first based on PbS and PbSe QDs,
and currently on lead halide perovskite QDs, with current performances $>16\%$,[39] in QDSSCs Pb and Cd-free QDs play currently a major role since most recent PCE records have been obtained with “green” QDs. This fact also represents an advantage with respect to the solution processed halide perovskite solar cells (PSCs), where PSCs presenting PCE exceeding the record for QDSSCs are always based on Pb halide perovskites.[40] However, PSCs present outstanding record PCE $\geq 25\%$.[41]

QDSSCs also present another interesting advantages. Very recently Klimov and co-workers have reported that in QDSSC configuration trapped photogenerated carriers can be partially recovered, and consequently recycled to ultimately contribute to the device efficiency.[38] They compared QDSSCs sensitized with colloidal ZCISe QDs attached to the TiO$_2$ using different capping providing them different binding interaction with TiO$_2$ and different steric hindrance. They show that similar performance can be obtained with different capping providing both weak and strong binding interaction with TiO$_2$, but lower performance was obtained for capping with strong steric hindrance as reduce the QD loading. Despite, in samples with weak binding interaction, most of the photogenerated carriers are trapped in QD shallow states, they can be later injected into the TiO$_2$ conduction band, contributing to the final device performance, if the trap lay above (below) the ETM (HTM) conduction (valence) band, see Figure 2a. In the same line, QDSSCs have a good tolerance to QD size dispersion as bigger QDs, with narrower QDs, can still injecting into ETM (HTM) if the conduction (valence) band lay above (below) the conduction band of the ETM (the redox level), see Figure 2b. This property confers an advantage of QDSSCs in comparison with thin-film colloidal QD solar cells where both traps and size distribution affect deleteriously the device transport properties, see Figure 2c. These result not just highlight the potentiality of QDSSCs to bypass the transport constrains arisen from traps and size distribution, but also point out again the increase of QD loading as a key aspect to improve QDSSC performance.

Beyond the QD loading, QDSSCs face a second key challenge, the device stability. This challenge has received significantly lower attention than the QD loading probably because QDSSCs did not present, at the first stages, enough performance and the research community focused first on this issue. However, nowadays when PCEs have surpassed the 13% in the same range than DSSCs, the stability of this devices requires more attention than historically received. Stability was the most important problem during the first steps of this technology as the iodine/iodide redox couple commonly used for DSSCs affects most of the semiconductors corroding them in few minutes. However, previous works pointed out that polysulfide redox provide longer stability to semiconductors in liquid electrolytes[16] and this is the redox system that most extensively has been used in standard and in record QDSSCs.[24,29–31] Despite, this redox system has allowed the QDSSCs evolution PCE from $<1\%$ to $>13\%$, it is far to be an optimum choice. While for sealed samples stored under dark[42] or room light,[43] 1000 h stability has been reported, for samples...
analyzed under 1 sun illumination there is no report\textsuperscript{24} of negligible degradation for >30 h.\textsuperscript{44} Polysulfide electrolyte limits the long-term stability via oxidation of the QDs.\textsuperscript{38} In addition, the oxidation of Cu in the brass electrode, also extensively used in combination with polysulfide system,\textsuperscript{16} upward the redox level, limiting the open circuit potential, $V_{oc}$.\textsuperscript{38} While carbon electrodes have provide interesting results in terms of efficiency,\textsuperscript{34,37,38} the stability in combination with polysulfide is severely limited.\textsuperscript{38} Consequently, the future applicability of QDSSCs will depend on getting a compatible semiconductor QD, redox, and counter electrode system stable beyond polysulfide.

An interesting alternative could be all-solid devices. However, in this case performance is limited, as just thin electrodes, <2 µm, can be employed to avoid hole transport loses in the solid HTM,\textsuperscript{45} in comparison with the ≈30 µm thick mesoporous photoanodes used in liquid QDSSCs.\textsuperscript{29} Thinner electrodes undoubtedly would limit the QD loading but still interesting for other applications as semitransparent or colored solar cells. Very recently it has been reported PCE >7% for all-solid QDSSCs using CH$_3$NH$_3$PbI$_3$ perovskite as sensitizer,\textsuperscript{46} see Figure 3a. In fact, the first report on halide perovskite for solar cell applications was with QDSSC configuration.\textsuperscript{47} By the
control of the precursor concentration, it is possible to deposit halide perovskite QDs decorating the mesoporous TiO2 surface, see Figure 3a. It has been demonstrated that in this conditions, without coalescence between the perovskite nanoparticles, the system using spiro-OMeTAD as HTM behaves as a classic QDSSC.[46,48] All-solid perovskite QDSSCs are semitransparent system using spiro-OMeTAD as HTM behaves as a classic cell stability perovskites, photoconversion efficiency, quantum dots, solar cells, solar

Keywords

The author declares no conflict of interest.

Acknowledgements

Financial support from the European Research Council (ERC) via Consolidator Grant (724424—No-LIMIT) and Generalitat Valenciana via Prometeo Grant Q-Devices (Prometeo/2018/098) is gratefully acknowledged.

Conflict of Interest

The author declares no conflict of interest.

Keywords

perovskites, photoconversion efficiency, quantum dots, solar cells, solar cell stability

Received: May 28, 2020
Revised: July 2, 2020
Published online: July 26, 2020
[31] H. Rao, M. Zhou, Z. Pan, X. Zhong, J. Mater. Chem. A 2020, 8, 10233.

[32] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, Science 2011, 334, 629.

[33] a) P. K. Santra, P. V. Kamat, J. Am. Chem. Soc. 2013, 135, 877; b) D. Esparza, T. Lopez-Luke, J. Oliva, A. Cerdán-Pasarán, A. Martinez-Benítez, I. Mora-Seró, E. D. I. Rosa, Electrochim. Acta 2017, 247, 899.

[34] W. Wang, W. Feng, J. Du, W. Xue, W. Zhao, L. Zhang, L. Zhao, Y. Li, X. Zhong, Adv. Mater. 2018, 30, 1705746.

[35] V. M. Blas-Ferrando, J. Ortiz, V. González-Pedro, R. S. Sánchez, I. Mora-Seró, F. Fernández-Lázaro, Á. Sastre-Santos, Adv. Funct. Mater. 2015, 25, 3220.

[36] Z. Pan, I. Mora-Seró, Q. Shen, H. Zhang, N. Li, K. Zhao, J. Wang, X. Zhong, J. Bisquert, J. Am. Chem. Soc. 2014, 136, 9203.

[37] a) J. Du, Z. Du, J.-S. Hu, Z. Pan, Q. Shen, J. Sun, D. Long, H. Dong, L. Sun, X. Zhong, L.-J. Wan, J. Am. Chem. Soc. 2016, 138, 4201; b) S. Jiao, J. Du, Z. Du, D. Long, W. Jiang, Z. Pan, Y. Li, X. Zhong, J. Chem. Phys. Lett. 2017, 8, 559.

[38] J. Du, R. Singh, I. Fedin, A. S. Fuhr, V. I. Klimov, Nat. Energy 2020, 5, 409.

[39] M. Hao, Y. Bai, S. Zeiske, L. Ren, J. Liu, Y. Yuan, N. Zarrabi, N. Cheng, M. Chasemi, P. Chen, M. Lyu, D. He, J.-H. Yun, Y. Du, Y. Wang, S. Ding, A. Armin, P. Meredith, G. Liu, H.-M. Cheng, L. Wang, Nat. Energy 2020, 5, 79.

[40] A. K. Jena, A. Kulkarni, T. Miyasaka, Chem. Rev. 2019, 119, 3036.

[41] M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshida, N. Kopidakis, A. W. Y. Ho-Baillie, Prog. Photovolt: Res. Appl. 2020, 28, 3.

[42] X. Zhang, X. Huang, Y. Yang, S. Wang, Y. Gong, Y. Luo, D. Li, Q. Meng, ACS Appl. Mater. Interfaces 2013, 5, 5954.

[43] Y. Yang, L. Zhu, H. Sun, X. Huang, Y. Luo, D. Li, Q. Meng, ACS Appl. Mater. Interfaces 2012, 4, 6162.

[44] J. Du, X. Meng, K. Zhao, Y. Li, X. Zhong, J. Mater. Chem. A 2015, 3, 17091.

[45] F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S. M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 2009, 131, 558.

[46] S.-M. Yoo, S.-Y. Lee, E. Velilla Hernandez, M. Kim, G. Kim, T. Shin, M. K. Nazeeruddin, I. Mora-Seró, H. J. Lee, ChemSusChem 2020, n/a.

[47] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J. Am. Chem. Soc. 2009, 131, 6050.

[48] S.-M. Yoo, S. J. Yoon, J. A. Anta, H. J. Lee, P. P. Boix, I. Mora-Seró, Joule 2019, 3, 2535.

Iván Mora-Seró (Ph.D. Physics 2004) is researcher at Universitat Jaume I de Castelló (Spain). His research is focused on crystal growth, nanostructured devices, transport and recombination properties, photocatalysis, characterization and development of photovoltaic and optoelectronic devices. Recent research activities are focused on new concepts for photovoltaic conversion and light emission (LEDs and light amplifiers) based on nanoscaled devices and semiconductor materials following two main lines: semiconductor quantum dots and halide perovskites.