



## Quantum-sized nanomaterials for solar cell applications



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### ABSTRACT

To date, the development of clean and sustainable energy sources has been a central focal point of research, supporting the worldwide rising demand for energy along with associated environmental concerns. The abundance of solar energy on the surface of the earth and its popular appeal makes it a promising candidate to comply with long-term energy demands. In this article, we provide a comprehensive review on different generations of solar cell based on the technological and economic aspects. The focus is on nanomaterial-based solar cells such as quantum dot sensitized solar cells (QDSSCs), a new PV mechanism that offers a new pathway for controlling energy flow. Over the past few years, a significant improvement has been achieved in the energy conversion efficiency (ECE) of QDSSCs (e.g., from 1% to beyond 11%). As such, they are a very promising alternative to conventional crystalline and thin film PV technologies due to their low cost, easy fabrication, and high performance. This review highlights the progress of QDSSCs along with future scope of innovative graphene structures, e.g., graphene-semiconductor nanomaterial (G-SNM), graphene-carbon nanotubes (G-CNT), and graphene-metal nanomaterial (G-MNM) hybrids in PV cells. In addition to graphene, we discuss other 2D materials that have remarkable optoelectronic properties for PV devices. The ECE of green QDSSCs (~11.61% certified) is now approaching that of dye-sensitized solar cells (~13%) through the technical advancement of many counterparts (e.g., photo-electrodes, sensitizers, electrolytes, and counter electrodes). Therefore, QDSSCs exhibit sufficient potential for future research focusing on the development of highly efficient solar cells.

### 1. Introduction

Over the time, due to gradual and inescapable depletion of available energy sources like fossil fuels, it has become very difficult to support

the energy demands that have increased exponentially worldwide. Moreover, to resolve the issues associated with global warming and greenhouse gases emission, it is of primary task to focus on the development of renewable energy sources, e.g., solar, hydro, wind,

*Abbreviations:* Ag, silver; Ag<sub>2</sub>S, silver Sulfide; AIST, Japanese National Institute of Advanced Industrial Science and Technology; AM, air mass; a-Si, amorphous silicon; Au, gold; AZO, Al-doped ZnO; Bi<sub>2</sub>S<sub>3</sub>, bismuth(III) sulfide; CB, conduction band; CBD, chemical bath deposition; CdHgTe, cadmium mercury telluride; c-Si, crystalline silicon; CdS, cadmium sulfide; CdSe, cadmium selenide; CdTe, cadmium telluride; CIGS, copper indium gallium selenide; CO<sub>2</sub>, carbon dioxide; CoS, cobalt sulfide; CPVT, National Centre of Supervision and Inspection on Solar Photovoltaic Products Quality, China; CuInS<sub>2</sub>, copper indium sulfide; CuS, copper mono-sulfide; Cu<sub>2</sub>S, copper(I) sulfide; CVD, chemical vapor deposition; CZ, Czoehrlanski; DSSCs, dye-sensitized solar cells; ECE, energy conversion efficiency; ECUST, East China University of Science and Technology; FF, fill factor; FhG-ISE, Fraunhofer Institute for Solar Energy System; FTO, fluorine-doped tin oxide; GaAs, gallium arsenide; Ga<sub>2</sub>O<sub>3</sub>, gallium(III) oxide; G-CNT, graphene-carbon nanotube; Ge, germanium; G-MNM, graphene-metal nanomaterial; G-SNM, graphene-semiconductor nanomaterial; GQDs, graphene quantum dots; HIT, heterojunction-with-intrinsic-thin layer; IBM, International Business Machines Corporation; InAs, indium arsenide; InP, indium phosphide; InSb, indium antimonide; IPCE, incident photon to current efficiency; ITO, indium-doped tin oxide; J<sub>SC</sub>, current density; KRICT, Korea Research Institute of Chemical Technology; LSPR, localised surface plasmon resonance; MAI, methylammonium iodide; MC, mesoporous carbon; MEG, multiple exciton generation; Mn, manganese; MoS<sub>2</sub>, molybdenum disulfide; MWCNTs, multi-wall carbon nanotubes; Nb<sub>2</sub>O<sub>5</sub>, niobium pentoxide; NIM, National Institute of Metrology, China; NiS, nickel sulfide; NREL, National Renewable Energy Laboratory; OTE, optically transparent electrodes; P<sub>in</sub>, input light irradiance; PbS, lead sulfide; PbSe, lead selenide; PL, photoluminescence; Pt, platinum; PV, photovoltaic; QD, quantum dot; QDSSCs, quantum dot sensitized solar cells; rGO, reduced graphene oxide; Sb<sub>2</sub>S<sub>3</sub>, antimony(III) sulfide; Si, silicon; SILAR, successive ionic layer absorption and reaction; SiO<sub>2</sub>, silicon dioxide; Sn, tin; SnO<sub>2</sub>, tin dioxide; SPR, surface plasmon resonance; S-Q, Shockley-Queisser; TBAI, tetrabutylammonium iodide; TGA, thioglycolic acid; Ti, titanium; TiO<sub>2</sub>, titanium dioxide; TMDs, transition metal chalcogenides; U & T, University of Toronto; V<sub>OC</sub>, open-circuit voltage; VB, valence band; WS<sub>2</sub>, tungsten disulfide; ZnO, zinc oxide; ZnO/G, zinc oxide/graphene; ZnSe, zinc selenide; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional

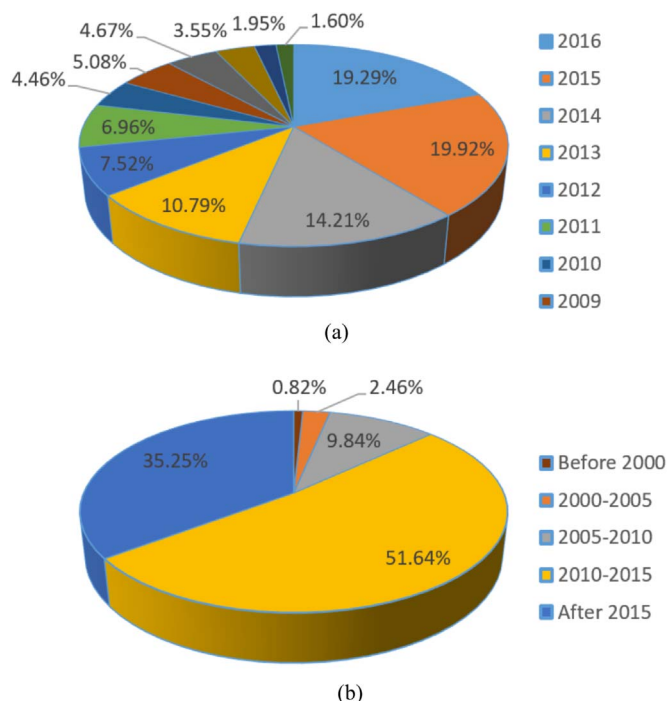
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**Fig. 1.** Pie charts including the basic statistics of publications related to this research: (a) total number of publications (N=1436) with the title topics including “quantum dots” and “solar cells” based on WorldWideScience data accessed on December 28, 2016 and (b) number of publications (N=244) cited in this review.

tidal, ocean, and geo-thermal energy.

Among all these renewable energy sources, solar photovoltaic (PV) technology is one of the most popular options in terms of cost-effectiveness, easy fabrication, and environmental friendliness. The PV technology involves two basic functions: (i) generation of charge carriers in light-sensitive materials from incident photons, and (ii) separation of the charge carrier using electrodes for conduction [1]. First in 1991, a dye-sensitized solar cell (DSSC) was proposed and assembled by O’Regan and Grätzel [2]. Over the time, this DSSC technology has gained considerable attention due to its roll-to-roll fabrication process with high conversion efficiency (e.g., ~13%) [3]. However, several parameters that restrict the commercialization of

DSSCs, are as high cost, fussy synthesis of organic dyes, and their chemical stability. Using quantum dots (QDs) as an alternative to molecular dyes is very promising due to their low-temperature solution processing, excellent tunable bandgap properties with quantum confinement effect, multiple exciton generation (MEG), and higher absorption coefficients. In Fig. 1(a), a pie chart is drawn to describe the basic statistics based on the number of publications with topic titles containing “quantum dots” and “solar cells” (N=1436, source: WorldWideScience data). Likewise, Fig. 1(b) presents such statistical results only for the publications cited in this review (N=244).

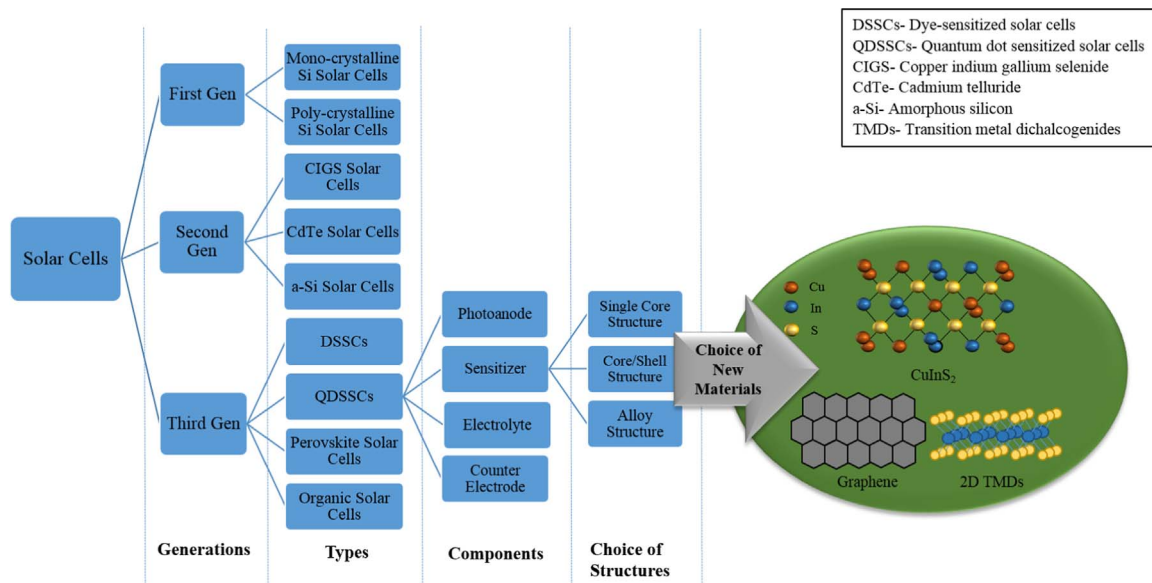
In this review, we provide an in-depth discussion on different generations of solar cells, with an emphasis on the incorporation of nanomaterials. This review focuses on bringing together the latest research that has aimed to enhance the performance of QDSSCs, with thorough discussion of photoanodes, sensitizers, redox electrolytes, and counter electrodes. We addressed the high optoelectronic and photocatalytic properties of graphene, other 2D materials, and hybrid systems in the realization of ultra-thin film PV devices. A comparative performance analysis is also carried out for the most recent QDSSCs, which differ in terms of material selection and tactics. Lastly, conclusions and future perspectives are also drawn.

## 2. The generation of solar cells and associated characteristics

The developmental history of solar cells can be broadly classified into three different generations, as shown in Fig. 2.

First generation PV cells are based on mono-crystalline silicon wafers (150–300 nm thick). The highly ordered atomic structure of crystalline Si (c-Si) grants them relatively high ECE (~25%), making them the first most common PV cell [4]. However, the high manufacturing cost and sophisticated processing steps of mono-crystalline Si cells necessitated the use of poly-crystalline Si at the expense of solar ECE. The crystalline Si solar cells offer the best reliability with the least efficiency degradations (e.g., over a period more than 25 years) [5]. The efforts to reduce manufacturing costs and recombination losses, and the emergence of new sophisticated technological steps gave birth to the next generation of solar cells.

The second generation of solar cells based on thin film technology offers cost reduction in manufacturing procedure, especially with respect to material savings and low (ambient) temperature processing



**Fig. 2.** Schematic representation of solar cell technology. The solar cell technology has been classified into first, second, and third generations. These generations are further classified into different types based on sensitizer material used for the fabrication of a solar cell.

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