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Recent progresses in solar cells: Insight into hollow micro/nano–structures

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ABSTRACT

The performance of third-generation solar cells is primarily a function of greater light harvesting, fast and facile charge transport, and limited charge recombination. Hollow micro/nano–structures have attracted considerable attention from the scientific community in recent decades due to their excellent multi–reflection and efficient scattering of incident sunlight, easy accessibility of inner spaces to electrolytes through meso/micro–channels in shells, and fast re–generation of reduced/oxidized species at the interface of sensitizer/electrolyte and electrolyte/counter electrode. This review aims to elaborate the application of hollow materials in photovoltaic cells.

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1. Introduction

Solar cells have gained considerable attention recently in a number of markets and are recognized as a better option for energy generation than conventional devices offering a clean, sustainable, and renewable green approach to electricity generation and possessing the potential to be an alternative to fossil fuels. After their invention by Grätzel [1], the third generation of solar cells has extensively developed due to low-cost, simple cell assembling and clean energy production. Dye–sensitized solar cells (DSSCs) and quantum dot–sensitized solar cells (QDSSCs) are examples of this latest generation. Although silicon-based solar cells have a higher conversion efficiency than other generations of solar cells, their high cost and complicated fabrication process have driven scientists and technologists to seek cheaper and simpler alternatives [2]. In silicon-based solar cells, a silicon semiconductor absorbs incoming light and transports photogenerated electrons to an electron collection electrode. However, in third

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generation solar cells, the light is absorbed by sensitizers (dye or QD) and charge transport is performed by semiconductors [3]. DSSC is more similar to the principle of plant photosynthesis than other types of solar cell (first– and second–generation).

Photovoltaic (PV) cells generally consist of a photoanode, sensitizer, electrolyte, and a counter electrode. A thin film of porous crystalline semiconductor (e.g. TiO_2, ZnO, SnO_2, etc.) coated on the surface of transparent conducting oxide (TCO) glass as a photoanode is used as a host for the incorporation of a sensitizer (e.g. dye, QD). A redox couple electrolyte (e.g. I^-/I_3^-, S^{2-}/S_x^{2-}, Co^{2+}/Co^{3+}) is used in the interface between photoanode and counter electrode (e.g. Pt, Au, carbon, etc.) to allow charge transport between them [4]. In solar cells, a dye-anchored semiconductor absorbs the incident sunlight at a wide range of wavelengths and produces electron/hole pairs by the excitation of electrons from the highest occupied molecular orbitals (HOMO - ground state) to the lowest unoccupied molecular orbitals (LUMO - excited state) of the dye molecules. The use of dye with a broad absorption band allows the harvesting of large quantities of sunlight [5]. The photo-generated electrons inject into the conduction band of the semiconductor and then make their way within interconnected semiconductor particle layers towards the TCO and to the outer circuit [6]. The band-gap structure of the semiconductor should match that of the dye. Moreover, oxide semiconductors show photocatalytic activity when they have large band-gaps [7]. The oxidized excited dye molecules regenerate in contact with the reducing species of the electrolyte by a reduction reaction. The reduced electrolyte species then oxidize by their redox couples. The electrons from the external circuit pass into the oxidized electrolyte via the counter electrode (CE) to regenerate the electrolyte redox couple. Finally, the transport of electron current to the outside of the cell through TCO glass produces electricity in an external circuit. The intrinsic function of TCO in charge collection (from injected photo–generated electron) and its low transmittance of the infrared spectrum notably affects the performance of the solar cells. TCOs are usually fabricated from a thin film of metal (e.g. Au, TiN) or doped-semiconductor with wide band–gap (e.g. In, Sn, Zn) [8]. In general, there is a continuous electron current in whole cell components. The efficiency of energy production of the cell depends greatly on the performance of each cell component.

To improve cell efficiency, a comprehensive study on the development of new materials, and cell types and cell module architectures is required. Many efforts have been made to enhance photo-to-electrical conversion efficiency and to reduce costs through the design of different materials, with variation in structure, composition, size, shape, morphology, surface area and porosity, and also fabrication technique. The utilization of low density photoactive materials coated onto a flexible polymeric substrate has been also introduced for the fabrication of lightweight solar cells [9]. Other attempts have been made in this fashion, such as employing “wet chemistry” preparation of active materials and cell assembly in ambient conditions compared to the use of high temperatures and vacuum conditions in the fabrication of first and second-generation solar cells. Although the development and improvement of photovoltaic cells has progressed rapidly, there are still some challenging limitations to address, such as the stability of different cell components for long-term usage. The short lifetime of solar cells, arising from factors that include photo–degradation of dye molecules, leaking and electrolyte sealing problems, inefficient charge transportation and charge exchange between dye, semiconductor, electrolyte and CE are major causes of lower efficiency in fabricated cells compared to the theoretical predicted efficiency value of 31%. The highest efficiencies recorded so far are 12% for small cells and 9% for mini–modules with reasonable stability for 1000 h at 80 °C (durable efficiency of 8–9%) [4]. On the other hand, the kinetic energy of charge transport is important for efficient cell performance. A higher rate of electron injection into the semiconductor conduction band than charge relaxation of excited electrons to the ground state, and a higher rate of reduction of oxidized dye by electrolyte than charge recombination both lead to an enhanced current density. Charge recombination is a limiting phenomenon in charge transfer that results it reduced charge collection in the TCO glass substrate. In fact, electron recombination consumes injected electrons through charge recapture by oxidized species (oxidized dye molecules or oxidized components of the electrolyte), resulting in fewer electrons available to be collected by TCO [10]. Another big challenge for solar cells is poor light harvesting efficiency due to low absorption efficiency in the red region. It is reported that 60% of the sunlight corresponding to the red and near-infrared regions cannot be absorbed by the sensitizer [11,12]. Thus, applying a material to scatter incident light can efficiently improve light absorption in the red region, producing more photo-induced electrons.

Submicrosphere hollow structures can provide higher light scattering and a larger surface area than corresponding solid particles of the same size. Hollow structures at a micro/nano scale have an empty cavity inside the particles that is supports different applications in area of catalysis: micro/nano reactor, chemical sensors and biosensing, photonic devices, energy storage, biomedical [13]. The structure, morphology, and composition of hollow materials can be tuned by varying effective parameters and reaction conditions. Submicrosphere hollow structures have also found many applications in energy conversion systems [14] due to their large surface area, low density, good surface permeability, high loading capacity, and controllablility (size, crystallinity, shell thickness, pore size/shape) [15]. The main advantages of hollow structures for solar cells are: higher light scattering through multi-reflection of incident light by hierarchical porous hollow shells, and better charge transport and short transport length by penetration of electrolyte into the hollow space [12]. Shell size, thickness, and number are parameters that affect electron transportation [12]. In this review, we focus on the application of interesting and versatile hollow spheres (HSs) in the development of solar cells. The effect of hollow structures in the performance of different components, such as photoanode, electrolyte and counter electrode will be discussed. In addition, it will be found that, in hollow structures, the morphology (e.g. spherical, cubic, spindle, etc.), composition (single component vs. composite materials: [e.g. ZnO vs. Ti/ZnO]), shell thickness, size distribution, and number of shells, determine the main cell parameters (current density, voltage, fill factor and efficiency). This review of the potential applications of hollow structures in photovoltaic cells will address two main issues: the important factors which need to be improved to enhance the cell performance, and the real and current challenges in fabrication of hollow structures.

The first reported work in this area was done by Fischer and coworkers in 2003 [16], when deposition of a chalcopyrite ($CuInS_2$ or $Cu(In,Ga)S_2$) layer with a thickness of 100 nm was carried out using a spray-ion layer gas reaction (ILGAR) process. The hollow spheres (HSs) were formed by crystal growth on the surface of droplets resulting from solvent evaporation, and used as a light harvesting material for thin film solar cells (second-generation). The Cu/In ratio, gallium addition, layer thickness, and process parameters (substrate and annealing temperatures) were effective in the formation of the hollow structures. The other cell components were Mo, CdS, ZnO, and Ni/Al as back contact, buffer layers, window, and front contacts, respectively. The following results were obtained for $CuInS_2$ prepared via a simultaneous process: a short-circuit current density (J_{sc}) of 7.8 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.594 V, a fill factor (*FF*) of 0.379, and an energy conversion efficiency (η) of 1.7%. For $Cu(In,Ga)S_2$, the mode of the deposition process affected the cell parameter results. The