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Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells

José Maçaira, Luísa Andrade, Adélio Mendes *

LEPAE—Departamento de Engenharia Química, Universidade do Porto—Faculdade de Engenharia, Rua Dr. Roberto Frias, s/n 4200-465 Porto, Portugal

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ABSTRACT

This work reviews the state-of-the-art nanostructured photoelectrodes for use in dye-sensitized solar cells. The influence of the photoelectrode structure in the DSC performance is analyzed. The nanostructured photoelectrodes can be classified into: (1) nanoparticles with high surface areas for efficient dye loading; (2) 1D nanostructures such as nanotubes and nanowires that offer direct electron transport pathways towards the collecting substrate; (3) 3D hierarchically ordered photoelectrodes that combine large pores for efficient electrolyte diffusion, large particles for effective light scattering but also small particles needed to achieve high surface areas; (4) 3D template-based techniques that create highly conductive macroporous scaffolds to produce structures with different length scales for electrolyte diffusion (macro and mesopores) and dye loading (micro and nanopores); and finally (5) hybrid TiO_2/graphene nanostructures able to suppress electron recombination in the semiconductor/electrolyte interface, increasing the electron mobility and extraction and also able to enhance light absorption, ultimately increasing the DSC performance.

Contents

1. Introduction

World energy consumption will increase 53% before 2035, driven not only by the economic growth and increasing population in developing countries but also by emerging economies such as China and India [1]. Relatively high oil prices, as well as concerns about the environmental impact of the fossil fuels combustion and strong government incentives have made renewables the fastest growing energy source according to the International Energy Outlook of 2011. The total renewable energy generation has increased 3.1% per year and it is expected to grow from 19%, recorded in 2008, to 23% in 2035 [2]. In particular, solar energy is the fastest growing segment of renewable energy sources, which in the non-OECD countries is expected to grow annually 22.8% until 2035. The forecasts for 2015 put total installed photovoltaic (PV) capacity in the world between 131 GW and 196 GW; 100 GW could be reached in 2013 [2].

Obviously, the PV market evolution will make use of the most competitive solar panels at the time, most likely the first

* Corresponding author. Tel.: +351 91 9889237.
E-mail address: mendes@fe.up.pt (A. Mendes).

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Nomenclature

V_{oc}	Open-circuit voltage, V
FF	Fill factor
I_s	Incident photon flux, $m^2\ s^{-1}$
J_{sc}	Short circuit current density, $A\ m^{-2}$
D_{eff}	Diffusion coefficient of electrons, $m^2\ s^{-1}$
L_f	Thickness of the TiO_2 film, m
L_n	Diffusion length, m
R_k	Recombination resistance, Ω
R_w	Transport resistance, Ω
FTO	Fluorine-doped SnO_2 conducting glass electrode
C_μ	Chemical capacitance
CB	Conduction band

Greek letters

η	Efficiency
α	Wavelength-dependent absorption coefficient, m^{-1}
τ_e^-	Electron lifetime, s
τ_{tr}	Electron transport time, s
η_{cc}	Collection efficiency

Subscripts

e^-	Electrons
I^-	Iodide
I_3^-	Triiodide
MPP	Maximum power point
OC	Open circuit
SC	Short-circuit

generation crystalline and polycrystalline silicon solar panels (c-Si). These devices at lab scale can achieve up to 25% sun to power conversion efficiency (PCE, η) and their recent progressively lowering prices reflects its industrial establishment that, undoubtedly, makes use of the today's semiconductor industry infrastructures. However, the high production and environmental costs led to a constant progress in the development and establishment of new PV technologies aiming to avoid the drawbacks of the c-Si solar panels. Some established semiconductor based technologies comprise gallium arsenide tin film solar cells (GaAs, η≈24%), copper–indium–galium–diselenide (CIGS, η≈20%), cadmium–telluride (CdTe, η≈17%) and amorphous/nanocrystalline silicon (η≈10%) solar cells [3]. This second generation of thin film technologies are believed to have an important role in the PV installation capacity by 2015 [2]. However, they also share the same performance and cost limitations as conventional Si devices. After approximately 20 years of research and development, third generation thin film solar devices are starting to emerge in the marketplace. This new generation of photovoltaic systems includes semiconductor quantum dots (QDPV, η≈6–10%) [4], organic semiconductors (OPV, η≈10%) [3,5] and dye sensitized solar cells (DSCs, η≈13%) [6]. These new technologies benefit from their low processing costs and environmental impact and thus short payback time when compared to the conventional solar devices. At present stage, third generation PV technologies are still far behind the efficiency values of the conventional Si-based solar cells (~20%); nevertheless, the promise of low processing costs and usage of available environmental-friendly raw materials make them subject to an intensive research and development.

Dye sensitized solar cells present themselves as a very promising photovoltaic technology. They are made of cheap components that are non-toxic and world-wide available and offer distinctive features such as semi-transparency, multi-color range possibilities, flexibility and lightweight applications but also good performance under low light conditions and different solar incident angles [7–9]. These unique characteristics open a new possibility of applications and markets where conventional solar devices will never be able to penetrate, *e.g.* low-power consumer electronics, outdoor or indoor recreational and BIPV applications. In fact, the DSC technology has recently been used by several companies in some commercial applications by Sony, Fujikura, Panasonic, G24i, Dyesol, 3G Solar and Toyota-Asin. However, for the DSC technology become a competitive alternative to the present PV technologies, major breakthroughs are necessary mainly concerning the two critical aspects of any PV device: power conversion efficiency and lifetime. Regarding the device lifetime, at least 25 years of constant power conversion efficiency should be guaranteed for outdoor applications. This aspect has caught researcher's attention in order to enhance DSCs' stability and thus many reports are being published concerning improvements on the stability devices and new sealing methods [10–15]. Several methods were proposed to enhance the efficiency of DSCs [6,16–18] being one of the most promising the use of nanostructured materials as photoelectrodes to enhance light harvesting and charge extraction to improve photocurrent, photovoltage and fill factor.

This work aims to review the state-of-the-art DSCs and mostly to demonstrate the influence of the photoelectrode structure in the DSC performance. Particular emphasis is given to nanostructured materials and cells, as well as their synthesis methods. This review discusses the various advantages of nanostructured DSC cells and the fact that a tailored design of the photoelectrode structure is crucial to control the charge extraction, to enhance light harvesting and to reduce charge recombination.

2. Operational principle of dye sensitized solar cells

In 1991 O'Regan and Grätzel proposed the first bulk heterojuntion photoelectrochemical solar cell with 7% power conversion efficiency, taking advantage of the 3D TiO_2 photoelectrode film and using a ruthenium dye as sensitizer [19]. DSCs mimic natural photosynthesis and differ from conventional p–n junction devices because light collection and charge transport are separated in the cell. Light absorption occurs in the chemisorbed sensitizer molecule, while electron transport occurs in the semiconductor anatase TiO_2—Fig. 1.

The photoelectrode is a mesoporous oxide layer composed of nanometer-sized particles. Attached to the surface of the oxide is a monolayer of dye responsible for light absorption. The optical absorbance that occurs in the dye molecules results in excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [20]. The photogenerated electrons are transferred to the conduction band of the semiconductor oxide and percolate through the