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Review article

A critical review of recent developments in nanomaterials for photoelectrodes in dye sensitized solar cells

C. Clement Raj, R. Prasanth*

UNESCO Madanjeet School of Green Energy Technology, Pondicherry University, Kalapet, 605014, India

HIGHLIGHTS

- Progress in photoanodes in recent years with nanostructured materials are reviewed.
- Novel fabrication techniques and its effects in efficiency has been systematically analyzed.
- Comparison of prominent materials such as TiO_2, ZnO and Nb_2O_5 have been carried out.
- Improvement methods for I_{sc} and V_{oc} for material systems have been analyzed.

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ABSTRACT

In a dye sensitized solar cell the photoanode performs a dual role of acting as a matrix for dye adsorption and as a charge transport medium for electron transport. The surface area and the electronic property of the material determine the current output of the device. So the performance of dye sensitized solar cell is significantly affected by our choice of material to be used as photoanode. High surface area, optimum carrier density, low impedance and efficient carrier transport are requirements for an efficient photoanode material in a DSSC. The goal of this review article is to highlight the fabrication methods used for the preparation of efficient nanostructured photoanodes. The application of these nanostructured photoanode materials and their impact on the device efficiency has been described in detail. The enhancement in the surface area of the material and its impact on the dye adsorption and current generation has been discussed. A detailed analysis of the role of different blocking layers used in improving the open circuit voltage of the device has been done. The outlook and future directions in improving the device performance are also discussed.

1. Introduction

Due to the ongoing industrialization and population growth the global demand for energy is estimated to double by the year 2050 [1]. There is an overwhelming concern over the environmental impact of coal based energy production, which is currently the major source of energy. Hence, the development of carbon-free sources of energy like Hydropower, Nuclear fission, Biomass, Wind, Geothermal, Solar and Ocean energy has gathered momentum in recent years [2]. Light from the sun is the most abundant and reliable source of energy. However, the cost and efficiency of solar energy production is the biggest barrier in shifting towards the environmental friendly and sustainable technology. Dye sensitized solar cell (DSSC) is one of the promising third generation photovoltaic technologies. The ease of fabrication, tunable optical properties for varied aesthetic sense and cost effectiveness has lead to meticulous research activities in this field. Fig. 1a shows the statistics of year wise increase in the number of publications related to dye sensitized solar cells. Fig. 1b depicts the year wise efficiency improvement in DSSC as well as other photovoltaic technologies. The first generation solar cells which are the conventional solar cells of today are based on Silicon. The efficiency of crystalline Si based solar cells have reached an efficiency of 25.6% for mono-Si and 20.4% for Poly-Si. The second generation solar cells are based on thin film technologies. Amorphous Si (10.1%), CIGS (20.5%), CdTe (19.6%) are some of the well established second generation solar cell devices. The third generation solar cell devices like Multi-junction (37.9%), DSSC (13%) and Organic (10.7%) are promising technologies that can surpass the Schokley Queisser limit [3]. The

* Corresponding author.
E-mail address: prasanth.get@pondiuni.edu.in (R. Prasanth).

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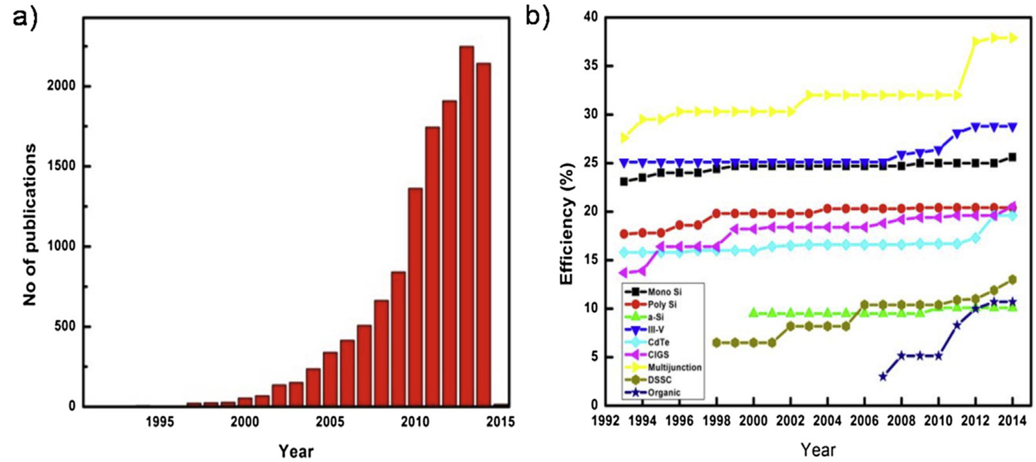

Fig. 1. (a) Number of publications per year by using dye sensitized solar cell as keyword for literature search (data source, Scopus) (b) Efficiencies reported for various solar cell technologies.

highest efficiencies of the different types of solar cells achieved so far have been listed in Table 1.

The market has growing interest in the third generation technologies due to their applicability to indoor facilities and in portable devices such as chargers, solar bags, and solar key boards. The ease of manufacturing and the ability to be seamlessly integrated with existing devices are factors which attracts industrial interest. The dye sensitized solar cell market is forecasted to grow over $130 million by the year 2023 [14]. The growth of DSSC in various market sectors are shown in Fig. 2a. The figure shows that the DSSC market which is confined only to portable electronics and disposable electronics is expected to take a huge leap in many other sectors.

Michael Gratzel and Brian O Regan made the remarkable discovery of dye sensitized solar cell in the year 1991 [5]. The DSSC is a simple photoelectrochemical cell that imitates the photosynthesis process in plants. The cell consists of a semiconductor based photoanode covered with a monolayer of dye (Fig. 2b). Photoexcitation of the dye results in the injection of an electron into conduction band of the semiconductor from the LUMO of the dye due to the overlap of the bands. The oxidized dye is then regenerated by the donation of an electron from the redox electrolyte during which I_3^- is converted to I^-. The reduction of the electrolyte species from I^- back to I_3^- by the addition of the electron at the platinum coated TCO completes the process. The open circuit voltage is determined by the difference between the Fermi level of the semiconductor and the redox potential of the electrolyte. The cell exhibits an overall light-to-electricity conversion efficiency of 7.1–7.9% [15]. The various charge transfer mechanisms and its respective time constants have been depicted in Fig. 3a. The dotted lines indicate the undesirable pathways that lead to losses due to recombination of charge carriers. The two main factors responsible for the effective charge separation are (i) The alignment of the conduction band of semiconductor with respect to the LUMO of the dye and (ii) the presence of large number energy states in conduction band of semiconductor than LUMO of dye molecule.

Table 1
List of highest efficiency of solar cells.

S. no	Classification	Area (cm^2)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF (%)	η (%)	Reference
1	Mono Si	143.7	0.74	41.8	82.7	25.6	[4]
2	Poly Si	242.74	0.6678	39.8	80	21.25	[5]
3	Amorphous Si	1.001	0.896	16.36	69.8	10.2	[6]
4	III-V	0.9927	1.122	29.68	86.5	28.8	[7]
5	CdTe	1.0623	0.8759	30.25	79.4	21	[8]
6	CIGS	0.9927	0.757	35.7	77.6	21	[9]
7	Multijunction	1.021	4.767	9.564	85.2	38.8	[10]
8	DSSC	1.005	0.744	22.47	71.2	11.9	[11]
9	Organic	0.993	0.793	19.4	71.4	11	[12]
10	Pervoskite	1.020	1.074	19.29	75.1	15.6	[13]

Through consistent research over the past twenty five years the efficiency of dye sensitized solar cells has reached a maximum of 13% [16]. In spite of drawbacks such as low efficiency and durability compared to conventional technologies, an interesting advantage of DSSC is that it can be seamlessly integrated with day to day low power gadgets [17]. Each component of the DSSC attracts widespread interest due to the fact that there is still room for improvement in the efficiency while bringing down the cost with the use of cheaper alternatives. A TCO layer with high transparency and minimum resistance can replace the existing expensive ITO/FTO coated glass [18]. A cheaper dye with a large absorption bandwidth can improve the absorption of light at the active layer [19]. An electrolyte that can provide higher open circuit voltage and stability is required [20–22]. A cheaper alternative material for platinum based counter electrodes with good conductivity and catalytic activity [23].

The semiconductor layer plays a major role in the functioning of the dye sensitized solar cell. An ideal photoanode materials must satisfy the following characteristics, A) A uniform nanostructured mesoscopic film with very high surface area for maximum dye adsorption, B) Maximum transparency such that it does not affect the light absorption of dye, C) Faster electron transport in order to minimize losses, D) The electron diffusion length of the material should be higher such that the thickness of the absorber layer can be increased and E) A porous photoanode that is completely accessible for the electrolyte [24]. Several conventional semiconductor materials such as Si, GaAs, InP and CdS have been found to decompose in solution due to photocorrosion in a DSSC. TiO_2, ZnO and Nb_2O_5 are found to be most promising photoanode materials. Various nanostructured materials like nanoparticles, nanorods, nanotubes, 3D Nanostructures, Nanopyramids and Nanopillars have been investigated for photoanodes in DSSC. The performance of the different nanostructured photoanodes in a dye sensitized solar cell is discussed in this article. The modifications in the photoanode and its resulting impact on the parameters like short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) is categorically examined.