Renewable and Sustainable Energy Reviews 82 (2018) 103–125

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

# Recent developments of graphene-$TiO_2$ composite nanomaterials as efficient photoelectrodes in dye-sensitized solar cells: A review

Foo Wah Low, Chin Wei Lai*

*Nanotechnology & Catalysis Research Centre (NANOCAT), Level 3, IPS Building, University of Malaya (UM), 50603 Kuala Lumpur, Malaysia*

ARTICLE INFO

*Keywords:*
Graphene
Titanium dioxide
Nanomaterials
Photoanode
Dye-sensitized solar cells

ABSTRACT

The energy demand is ever increasing on aspect of primary and secondary energy sources to fulfill the energy requirement in this century. High energy supply is required especially in the developing countries to sustain the lifestyle due to the growth in the world's population and techno-economic city. In fact, the sources of fossil fuel-based energy are limited and the use of fossil fuels can lead to the environmental pollution problem. Accordingly, the combustion of fossil fuels sources will give rise to the global warming issue, i.e., the greenhouse effect of carbon dioxide resulting in erratic weather patterns, such as floods, draughts, etc. In the last two decades, solar photovoltaic cells have been used as the alternatives to generate renewable, sustainable and green energy. High dye absorption rates, efficient charge separation of exciton, and free charge carrier formation as well as large area production at low costs contribute to the emerging photovoltaic technologies. Generally, the materials involved in photoanode section (acting as the platform for the electron collection) are the main key to produce high-efficiency photovoltaic cells. Currently, multijunction based solar panels showed the highest performance of 40% efficiency as compared to that of the conventional Si based solar panels with 22–27% efficiency. Apart of that, DSSCs sensitized by the silyl-anchor and carboxy-anchor dyes have attained the highest efficiency of 14%. In recent years, the metal doping or binary oxide photo-catalyst systems, particularly graphene-$TiO_2$ nanocomposites, have attracted much attention due to their extraordinary characteristics, i.e., (i) photocatalyst activity enhancement, and (ii) accelerated electron mobility to reduce the charge recombination. The high efficiency of the graphene-$TiO_2$ nanocomposites in DSSCs' reaction basically requires a suitable architecture that minimizes electron loss during excitation state and maximizes photon absorption. In order to further improve the immigration of photo-induced charge carriers during excitation state, considerable efforts have to be exerted to further improve the charge mobility and maximize the dye loading. It has also been reported that the properties of graphene-$TiO_2$ nanocomposites primarily depend on the nature of the preparation method, and the role of optimum dopants content incorporated into the graphene photoanode to improve the dye molecules loading and minimize the charge recombination. Therefore, we review recent achievements for different nanoarchitecture of $TiO_2$, as well as graphene-$TiO_2$ composite nanostructured based photoanode in DSSCs performance with future prospects and challenges. Indeed, graphene-$TiO_2$ composite photoanode has proven to be of great interest for use in DSSCs.

## 1. Introduction

Global warming resulting from the large-scale emission of carbon dioxide ($CO_2$) and expansion of the greenhouse effect is a critical topic of human concerned. The excess $CO_2$ in the atmosphere will form some kind of blanket, trapping heat radiating from the Earth towards the space and subsequently warming the planet [1]. In the past decades, continuous efforts, i.e., carbon capture and geological sequestration technologies, have been exerted to minimize the emissions of $CO_2$. However, these efforts required extraneous energy input [2]. It has also been reported that the assumed global demand for energy requirement will be doubled by the year of 2050 associated with the growth of population and industrialization, especially in developing countries [3]. Henceforth, the development of renewable energies with fossil fuels-free like wind [4], solar thermal [5], biomass [6], hydropower [7] as well as photovoltaic [8] energy have been widely studied in order to overcome the global issues. It is worth to mention that the natural renewable energy like solar energy can be converted into controllable and useful energy which is everlasting and potential damage/pollution free to the environment. Solar energy is also considered to be a large clean

* Corresponding author.
*E-mail address:* cwlai@um.edu.my (C.W. Lai).

http://dx.doi.org/10.1016/j.rser.2017.09.024
Received 22 May 2017; Received in revised form 28 August 2017; Accepted 6 September 2017
1364-0321/ 

**Table 1**
Performance of solar cell measured under AM 1.5 spectrum (1000 W/m$^2$).

| No. | Classification | Active Area, $A$ (cm$^2$) | Open Circuit Voltage, $V_{oc}$ (V) | Short Circuit Current Density, $J_{sc}$ (mA cm$^{-2}$) | Fill Factor, $FF$ (%) | Efficiency, $\eta$ (%) | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | Mono Si | 180.43 | 0.7438 | 42.25 | 83.8 | 26.3 ± 0.5 | Kaneka Corp. et al./2016, [11] |
| 2 | Poly Si | 242.74 | 0.6678 | 39.80 | 80.0 | 21.3 ± 0.4 | Zhang S. et al./2015, [12] |
| 3 | Amorphous Si | 1.001 | 0.896 | 16.36 | 69.8 | 10.2 ± 0.3 | Matsui T. et al./2013, [13] |
| 4 | III-V | 0.9927 | 1.122 | 29.68 | 86.5 | 28.8 ± 0.9 | Kayes B.M. Et al./2011, [14] |
| 5 | CdTe | 1.0623 | 0.8759 | 30.25 | 79.4 | 21.0 ± 0.4 | First Solar et al./2014, [15] |
| 6 | CIGS | 0.9927 | 0.757 | 35.70 | 77.6 | 21.0 ± 0.6 | Solibro et al./2014, [16] |
| 7 | DSSCs | 1.005 | 0.744 | 22.47 | 71.2 | 11.9 ± 0.4 | Komiya R. et al./2011, [17] |
| 8 | Organic | 0.992 | 0.780 | 19.30 | 74.2 | 11.2 ± 0.3 | Mori S. et al./2015, [18] |
| 9 | Perovskite | 0.9917 | 1.104 | 24.67 | 72.3 | 19.7 ± 0.6 | Yang W.S. et al./2015, [19] |

energy source. However, the production cost, device size, stability, repeatability, reproducibility, and also its efficiencies have yet to approach to the green and sustainable technology in future [3].

Generally, solar cells technology has three core generations. Silicon (Si) wafer based is categorized as the first generation or conventional solar cell. The second generation is thin film solar cell whereas the third generation is the latest emerging solar cell technologies like multijunction, organic, dye-sensitized (DSSCs), GaAs and thermo-photovoltaics (TPV) having the conversion efficiencies beyond the theoretical Schokley Queisser limit [9]. Specifically, Table 1 tabulates the solar cells performance, while Fig. 1 displays the solar photovoltaic technologies in terms of conversion efficiency. It is noteworthy that the multijunction solar panels composed of III-V and silicon material shows the highest efficiency and better stability compared to that of those in the market due to the n/p-type of semiconductor since its higher carrier mobilities and direct energy gaps. However, these multijunction solar panels have the limitations in terms of (i) huge size, i.e., 28 cm-squared with four-junction hybridization, (ii) costly materials used for production, (iii) fragile panel, and (iv) complex manufacturing as compared to that of other types of solar cells. On top of multijunction solar panels, Si-based solar cells, thin films solar cells, and III–V solar cells technologies have also received numerous attractions and attentions. However, these solar cells also suffer from shortcomings in terms of relatively high production cost, complex inner working panel, and time consuming. In 2017, Kaneka and co-researchers successfully fabricated large-area silicon solar cells combining interdigitated back contacts and an amorphous silicon/crystalline silicon heterojunction. with efficiency of 26.7% [10]. The authors claimed that essential device properties such as lifetime, series resistance and optical properties have been improved simultaneously by reducing recombination, resistive and optical losses. The main reason was attributed to the fabrication of a high quality silicon thin film heterojunction passivation technology and low-resistance electrodes. Furthermore, they also found that front side architecture contributed high Jsc, Voc, and FF value where is accumulation of light with small current loss whereas the role of rear side architecture of heterojunction solar cells was collection and optimization of photo-generated carriers with very low power loss.

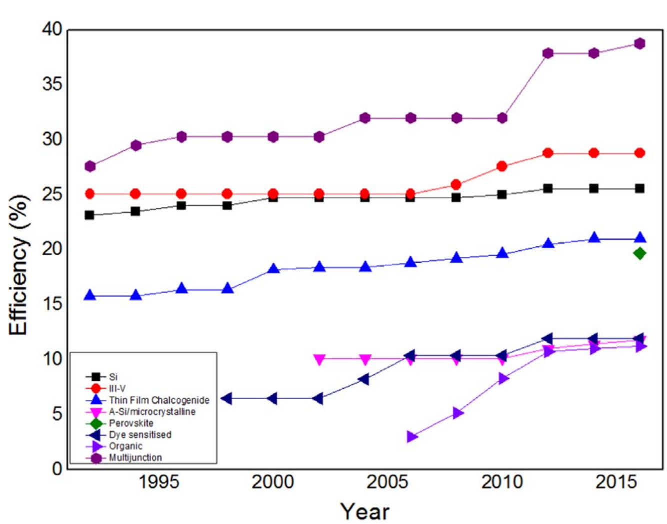


**Fig. 1.** Solar cells efficiency reported based on several technologies.

In late 19th century, DSSCs based mesoporous titanium dioxide ($TiO_2$) (third generation of photovoltaic technology) was first produced by Michael Grätzel and his co-workers at the Ecole Polytechnique Federale de Lausanne, Switzerland [20]. Accordingly, the combination of dyes injection concept (electric charge generation) with nanostructured electrodes in DSSCs has resulted in a good conversion efficiency ($\eta$) of ~7% [21]. Additionally, DSSCs are gaining considerable interest today devoted to the low material costs of the solar cells and abundantly available raw materials, as well as the low processing temperature of the solar cell technology. DSSCs can also be supplied as portable devices as well as can be used in indoor facilities such as chargers, solar key boards, and solar bags [3]. In 2006, Poortmans et al. reported that the durability of DSSCs is around 20 years. However, leakage is the main issue in liquid electrolyte based DSSCs [22].

Technically, DSSCs are generally considered as the solid-state photovoltaics or photo-electrochemical cells imitating the concept of plants' photosynthesis process. The core concept of DSSCs is photoanode covered by the dye sensitizer (refer Fig. 2). In DSSCs configuration, light is absorbed by the dye sensitizers and the charge carriers are transported to the wide band gap nanocrystalline semiconductor.

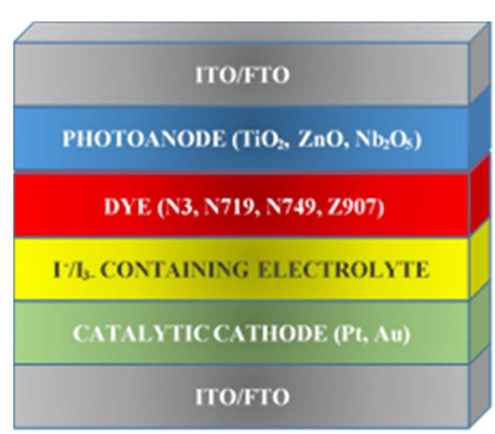


**Fig. 2.** Schematic diagram of DSSCs structure.