Nano Energy (2014) 4, 157–175

Available online at www.sciencedirect.com

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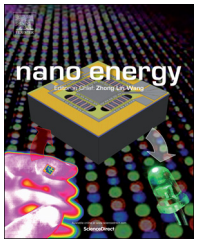
journal homepage: www.elsevier.com/locate/nanoenergy




REVIEW

# Carbon nanostructure counter electrodes for low cost and stable dye-sensitized solar cells

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Received 19 August 2013; received in revised form 17 October 2013; accepted 19 October 2013
Available online 1 November 2013

**KEYWORDS**
Dye-sensitized solar cells;
Counter electrodes;
Carbon nanostructures;
Charge transfer resistance

**Abstract**
Dye sensitized solar cells (DSCs) provide a low cost alternative to silicon solar cells due to their low material and fabrication cost. Usually DSCs utilize platinum to catalyze the iodine redox couple and complete the electric circuit. Since platinum is rare and expensive metal, nanostructured carbonaceous materials have been widely investigated as a promising alternative to replace it. Carbon nanostructures have shown significant properties such as high electrochemical activity, high corrosion resistance, and low cost which make them ideal for replacing platinum in the counter electrodes of DSCs. Here we reviewed the development in carbon based counter electrodes which utilize the advantages of high surface area and high electrocatalytic ability due to their nanostructured morphology. First, various carbon nanostructures including graphene, carbon nanotubes, carbon nanofibers, carbon nanoparticles, conductive carbon, carbon dye and composite carbon nanostructures are introduced. Second, carbon nanostructured counter electrode morphologies and their effects on DSC performance are discussed. Third, surface defects and their effects on cell performance are described. Finally, equivalent circuit models at the counter electrode-electrolyte interface are presented. This work will provide deep insights and guidance for researchers to design, develop and/or select carbon nanostructures for cost effective Pt-free or less-Pt loaded DSCs.


**Contents**



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http://dx.doi.org/10.1016/j.nanoen.2013.10.012

## Introduction

Energy has been the main driving force for the development of human civilization. So far the world energy demands are mainly met by fossil fuels (coal, petroleum, and natural gas). The main issue with fossil fuels is that they are nonrenewable and produce $CO_2$ and other greenhouse gases. Renewable sources like wind and hydropower avoid most of the problems with fossil fuels but they are both limited in sources and have high setup and maintenance cost [1–10]. Comparatively solar energy is a renewable and continuous energy source available in most part of the world and hence has received tremendous interest in recent years. It has the ability to produce clean energy and has the flexibility to be set up at the load locations like residential, industrial buildings, etc. avoiding any transmission cost and power losses [11].

Dye-sensitized solar cells (DSCs) based on wide bandgap meso-porous metal oxide that is sensitized by dye molecules were first introduced by Brian O'Regan and Michael Grätzel in 1991. DSCs were successful in imitating the natural process of photosynthesis to convert light to energy [12]. In contrast to the silicon-based solar cells which relied on high purity silicon with minimal defects, DSCs are prepared in simple laboratory environment without much concern on material purity and high temperature processing [12,13]. Thus, DSCs show potential as low-cost alternatives to silicon solar cells due to their lower fabrication and material cost [13,14]. Further DSCs provide possibility of numerous advantages like transparency or semi-transparency, flexibility, lightweight, and relatively high performance in diffuse light [13].

A typical DSC constitutes a photoanode and counter electrode (CE) with a redox electrolyte filled in between. The photoanode is usually a porous film of sintered $TiO_2$ nanoparticles deposited on fluorine-doped tin dioxide (FTO) sensitized by dye molecules, the CE is generally a platinum-coated FTO glass substrate. When dye molecules are illuminated with sunlight, photoelectrons are generated and then injected from the dye molecules to $TiO_2$, followed by traveling to the CE through an external circuit performing work. Finally, the electrolyte regains electrons from the CE, and the dye molecules recover lost electrons from the electrolyte [15–18]. The DSCs with the above device structure using an ($I^-/I_3^-$) redox electrolyte and Ru-based dyes achieved an energy conversion efficiency over 11% [19]. Also, DSCs with 12.3% efficiency were reported under simulated AM 1.5 global sunlight. This was achieved by replacing Ru-based dyes with a donor-π-bridge-acceptor zinc porphyrin (YD2-o-C8) as the sensitizer and substituting the conventional ($I^-/I_3^-$) redox with a Co (II/III) tris(bipyridyl)-based redox couple. The YD2-o-C8 porphyrin absorbs a broader spectrum of light across the visible solar spectrum, leading to a larger photocurrent generation than typical Ru-based dyes; while the combination of the Co (II/III) tris (bipyridyl)-based redox couple with YD2-o-C8 porphyrin significantly reduces the interfacial back electron transfer from $TiO_2$ to the oxidized cobalt mediator, leading to a high open circuit voltage ($V_{OC}$) close to 1 V [20,21].

Platinum has been extensively used in the CE of DSCs due to its high electro-catalytic nature and high conductivity [16,22,23]. However, platinum is an expensive and rare material that contributes significantly to the overall cost of DSCs [23,24]. Due to concerns of the high cost of platinum, carbonaceous materials like graphite, carbon black, carbon nanotubes, electrospun carbon nanofibers (ECNs), polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with p-toluenesulfonate (PEDOTTsO) or polystyrenesulfonate (PEDOT-PSS) have been investigated as potential low cost replacements for platinum [5,25–38]. Platinum in DSCs is generally deposited by sputtering or solution processing, which leads to planar deposition with little roughness and hence has a limited contact area with the electrolyte for charge transfer from CE to the electrolyte. On the other hand, carbonaceous materials can provide large effective surface areas due to their porous or rough morphology, leading to a large number of reduction sites and hence low charge transfer resistance. This however requires thickness of a few to tens of microns compared to few tens of nanometers for Pt. Due to large thickness and low conductivity of carbon compared to that of platinum, the resistance through the bulk of the carbon electrode and the high contact resistance of carbon with FTO can outweigh the reduction in charge transfer resistance which can lead to overall increase in series resistance [5,21].

In this paper, we review the development in carbon based counter electrodes which utilize the advantages of high surface area and high electrocatalytic ability due to their nanostructured morphology. First, various carbon nanostructures