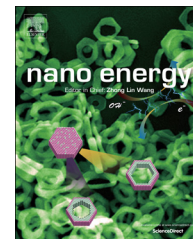




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RAPID COMMUNICATION

# Improved performance of dye solar cells using nanocarbon as support for platinum nanoparticles in counter electrode



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## Abstract

Carbon nanoparticles (CNPs) were used to support platinum nanoparticles as counter electrodes in dye-sensitized solar cells (DSCs). Carbon nanoparticles provided larger effective surface area and better exposure of Pt nanoparticles resulting in very efficient electrocatalytic performance as counter electrode. DSCs fabricated using such counter electrode showed enhanced efficiency owing to lower series resistance and higher fill factor as a result of reduced charge transfer resistance. The overall power conversion efficiency of the DSC devices using these CNP/Pt counter electrodes reached 8.12% as compared to 7.49% for reference platinum counter electrode DSCs under 1 sun illumination.

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## Introduction

Dye sensitized solar cells (DSCs) have been heavily investigated in the last two decades as a potential low-cost alternative to silicon solar cells due to their lower material and fabrication cost, and numerous other advantages such as transparency, flexibility, lightweight, and relatively higher performance in diffuse light and at higher temperatures [1–7]. These cells utilize dye molecules as sensitizers attached to a wide bandgap

mesoporous metal oxide and can successfully imitate the process of photosynthesis to convert light to electricity [8,9]. A typical DSC constitutes a working electrode or photoanode and counter electrode (CE) or cathode with a redox electrolyte injected in between. The photoanode is usually a porous film of sintered TiO<sub>2</sub> nanoparticles deposited on fluorine-doped tin oxide (FTO) and sensitized by dye molecules. TiO<sub>2</sub> nanoparticles can provide very high surface area for dye attachment and can scatter incident light efficiently for larger particle size [2]. The CE is generally a platinum-coated FTO glass substrate and the electrolyte is generally an iodide/triiodide redox couple. Upon light illumination, the dye molecules generate and inject photoelectrons into the TiO<sub>2</sub>. This is followed by the electrons traveling to the CE through an external circuit performing

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electric work and dye molecules regaining electron from the electrolyte. The electrolyte then regains electrons from the CE completing an electric circuit [1,2,8-11].

Platinum exhibits attractive properties such as high electrocatalytic nature and large conductivity and hence has been extensively used in CEs of DSCs. However, the high cost of platinum contributes significantly to the cost of DSC [12]. Therefore low cost carbon based materials including graphene, graphite, carbon black, carbon nanotubes, electrospun carbon nanofibers (ECNs), polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with p-toluenesulfonate (PEDOT-TSO) or polystyrenesulfonate (PEDOT-PSS) have also been heavily investigated as catalytic materials in the CE of DSCs [13-29]. Platinum based DSCs generally utilize sputter coating or spin coating to deposit Pt over FTO substrate and hence have more or less planar morphology with little roughness. This results in limited electrode-electrolyte interfacial area leading to lower number of reduction sites and significant charge transfer resistance which adds to the overall series resistance that limits device performance. Therefore, nanostructured carbonaceous materials with porous structures can provide comparatively large interfacial area with the electrolyte. This results in larger number of reduction sites and thus lower charge transfer resistance [10]. However, the thickness requirement of carbon CEs is generally much higher (few tens of microns) than Pt CEs (~40 nm) affecting overall cost [10,15,30]. Further, higher thickness introduces higher bulk resistance which along with the contact resistance between carbon and the FTO substrate also contributes to the overall series resistance [31]. This increase in bulk and contact resistance of the carbon CEs can overcome the decrease in charge transfer resistance leading to an overall increase in series resistance lowering performance of the device [10,15].

In this study, carbon nanoparticles were used to support platinum nanoparticles in the counter electrode of DSC. The composite structure had lower charge transfer resistance, comparable bulk resistance, and hence an overall lower series resistance leading to higher power conversion efficiency than conventional platinum based DSCs.

## Material and methods

### Preparation of counter electrodes

Carbon nanoparticles (Printex L, Degussa) were taken in a glass petridish and soaked in platinum precursor solution (0.02 M  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in anhydrous ethanol) for 6 h. The soaked nanoparticles were then heated in an oven at 400 °C for 15 min. After heating, the sample was mixed with a binder, carboxymethyl cellulose (CMC) sodium salt in DI water, to make a paste. The resulting paste was then doctor bladed onto an FTO glass substrate. The sample was then dried at 60 °C for 12 h.

For comparison, reference platinum counter electrode was fabricated by spin coating two layers of platinum precursor solution (0.02 M  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in anhydrous ethanol) on FTO glass substrate followed by heating at 400 °C for 15 min after each layer.

Scanning electron microscopy (SEM) images of the counter electrode was performed via Hitachi S-4300N SEM and

the energy dispersive X-rays spectroscopy (EDX) spectra were also obtained using this SEM.

The cyclic voltammograms (CVs) of counter electrodes were carried out in acetonitrile solution containing 10 mM LiI and 0.5 mM  $\text{I}_2$  using 0.1 M tetra-n-butylammonium tetrafluoroborate as the supporting electrolyte. Ametek VERSASTAT 3-200 Potentiostat with a frequency analysis module (FDA) was used for Cyclic Voltammetry measurements with reference electrode probe connected to an Ag/AgCl electrode and counter electrode probe connected to a thin platinum wire. The working electrode probe along with the sensor probe was connected to the electrode under test. A cyclic potential sweep was applied with initial and final voltages of -0.2 V and vertex voltage of 1.2 V. The scan rate was set to 0.05 V/s.

Electrochemical Impedance Spectroscopy was performed in dummy cells consisting of two symmetric electrodes facing each other with the electrolyte in the middle. Dummy cells were used as test devices to avoid the effects of photoanodes. Nyquist plots were obtained by probing the dummy cells with AC-signal using Ametek VERSASTAT 3-200 Potentiostat with a frequency analysis module (FDA). The AC-signal was set at a zero bias and AC-frequency was swept from 0.1 Hz to 100 kHz.

Tafel polarization plots were obtained by using Ametek VERSASTAT 3-200 Potentiostat with a frequency analysis module (FDA) and applying voltage from -1 V to 1 V at a scan rate of 0.005 V/s to the same dummy cell used in the EIS measurements to obtain the Tafel plots.

The thickness of the CNP/Pt electrode was measured by Dektak Profilometer.

### Fabrication of dye-sensitized solar cells (DSCs)

Photoanodes were fabricated by coating a compact  $\text{TiO}_2$  layer over FTO glass substrate via spin coating of a precursor made of titanium diisopropoxide bis(acetylacetonate) solution in anhydrous ethanol. This was followed by the deposition of  $\text{TiCl}_4$  treated nanocrystalline  $\text{TiO}_2$  layer (Solaronix Ti-Nanoxide HT/SP) and light-scattering layer (Dyesol WER4-0) by doctor blading. The photoanodes were sintered after deposition of each layer at 115 °C for 15 min and 475 °C for 45 min. The sintered photoanodes were then immersed in N719 dye solution containing 0.5 mM Ruthenizer 535-bisTBA dye (Solaronix N-719) in acetonitrile/t-butanol (volume ratio:1/1) for 24 h. Finally, the photoanodes were rinsed in acetonitrile for 2 h and blow dried with compressed nitrogen gas.

The photoanode and counter electrode were assembled together using a thermoplastic sealant (Meltonix 1170-60PF, Solaronix). The  $\text{I}^-/\text{I}_3^-$  electrolyte was made of 0.03 M  $\text{I}_2$ , 0.60 M 1-butyl-3-methylimidazolium, 0.10 M guanidine thiocyanate, and 0.5 M tert-butylpyridin in acetonitrile and valeronitrile (85:15 by volume), which was then injected into the cells. All devices were tested under AM 1.5 illumination with light intensity of 100 mW/cm<sup>2</sup>.

## Result and discussion

### 1.1. Morphological and elemental analysis

Figure 1a and b shows SEM image of carbon nanoparticles (CNPs) and CNPs supported Pt nanoparticles (CNP/Pt)

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