



Boron-doped carbon nanotubes as metal-free electrocatalyst for dye-sensitized solar cells: Heteroatom doping level effect on tri-iodide reduction reaction



Min-Hsin Yeh^{a,1}, Yow-An Leu^{a,b,1}, Wei-Hung Chiang^{c,*}, Yan-Sheng Li^c, Guan-Lin Chen^c,
Ta-Jen Li^a, Ling-Yu Chang^b, Lu-Yin Lin^d, Jiang-Jen Lin^{b,**}, Kuo-Chuan Ho^{a,b,***}

^a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^b Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

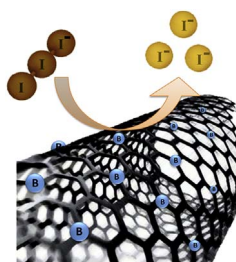
^c Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

^d Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan

HIGHLIGHTS

- B-doped carbon nanotube (BCNT) was used in dye-sensitized solar cells.
- BCNTs with various doping levels of boron were studied for the I_3^-/I^- reaction.
- BCNTs was synthesized by an atmospheric pressure chemical vapor deposition (CVD).
- Electrocatalytic ability of CNT can be increased significantly by doping B atom.
- B atoms act as the active sites by transferring charges to neighbor C atoms.

GRAPHICAL ABSTRACT



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ABSTRACT

Heteroatom-doped carbons have been substantially applied on electrochemical applications for their exceptional electrocatalytic ability and electric conductivity. Among the doping elements, electron-deficient boron (B) is considered to be a promising heteroatom for the chemical doping of carbon materials to modify the chemically inert sp^2 carbon structure and thus activate the abundant free-flowing π electrons. In this study, B-doped carbon nanotubes (BCNTs) with various boron doping atomic percentages (0.40–3.92 at%) are synthesized and used as an electrocatalyst on the counter electrode (CE) of dye-sensitized solar cells (DSSCs) for investigating the effect of boron doping on carbon materials. A solar-to-electricity conversion efficiency (η) of $7.17 \pm 0.11\%$ is achieved for a DSSC with a CE containing BCNTs with optimized B doping concentration (BCNT-0.40 at%), which is higher than that of the cells with CEs consisting of pristine carbon nanotubes (CNT, $\eta = 5.98 \pm 0.20\%$) and is comparable to that of the cell with a Pt CE ($\eta = 7.98 \pm 0.05\%$). It is also noteworthy from a practical viewpoint

* Corresponding author. Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan.

** Corresponding author. Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan.

*** Corresponding author. Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

E-mail addresses: whchiang@mail.ntust.edu.tw (W.-H. Chiang), jianglin@ntu.edu.tw (J.-J. Lin), kcho@ntu.edu.tw (K.-C. Ho).

¹ These authors contributed equally.

that the developed atmospheric-pressure synthesis method for synthesizing BCNT is amenable to industrial-scale production since a requirement for vacuum system can be avoided.

1. Introduction

Carbonaceous materials have been widely researched as an alternative choice to replace noble metallic catalysts in various electrochemical fields mainly because of their exceptional electrical conductivity, reasonable chemical durability, and promising electrocatalytic ability [1–6]. These carbon materials provide a solution to replace expensive metals and to reduce the cost of pertinent devices; they also enhance the performance and durability of the devices. Due to these advantages, carbon materials have also been introduced successfully in the field of dye-sensitized solar cell (DSSC) as a Pt-free catalyst in the part of the counter electrode (CE). A CE in a DSSC plays a role for collecting electrons from the photoanode and reducing triiodide ions (I_3^-) to iodide ions (I^-) at the CE/electrolyte interface. Conventionally, a Pt layer coated conducting glass was used as the CE in a DSSC, due to its outstanding electrocatalytic ability for I_3^- reduction and proven chemical durability in severe circumstances [7]. Several carbonaceous materials, e.g., activated carbon [8], carbon black [9], graphite [10], carbon nanotube [11–13], graphene [14–16], graphene nanoribbon [17], graphene aerogels [18], carbon nanotube/graphene aerogels [19], and conductive polymer coated graphene [20], have become potential materials to substitute Pt; this is mainly attributed to their intrinsic properties of low cost, high conductivity, and reasonable electrocatalytic ability for the reduction of I_3^- ions. Nevertheless, the performance of DSSCs with carbon based CE is still not good enough to achieve the same level as that with Pt based CE, due to its innate characteristics of few active sites on chemical inert sp^2 carbon structure for catalyzing I_3^- ions reduction reaction.

To further increase the number of active sites on the carbon surface and enhance their electrocatalytic activity, chemical doping of carbonaceous materials with heteroatoms is one of the most efficient approaches to tailor their electronic and chemical properties, thus changing their electrocatalytic characteristics [21,22]. It has been reported that the electrocatalytic ability of carbonaceous materials could be improved by incorporating different heteroatoms due to the electronic structure modification by heteroatomic dopants [23–29]. Among various doping elements, electron-deficient boron (B) is considered to be a promising candidate for the effective chemical doping of carbon materials since it has only three valence electrons, allowing it to functionalize the chemically inert sp^2 carbon structure and initiate the abundant free-flowing π electrons and act as catalysts for electrochemical applications. Moreover, the addition of B could significantly improve the conductivity of carbon materials by increasing the density of hole-type charge carriers [30,31]. These merits enhance the electrocatalytic ability of carbons for reducing I_3^- ions in the case of DSSC application [32]. However, there is no report investigating the effect of boron dopant concentrations in carbonaceous materials on the electrocatalytic ability for catalyzing I_3^- ions reduction reaction and how it influences the performance of the pertinent DSSCs. In fact, the main difficulty is caused by lacking some efficient processes to precisely control the boron dopant concentrations on the carbon surface [33–35].

In this study, B-doped carbon nanotubes (BCNTs) with different boron dopant concentrations (0.40–3.92 at%) were successfully synthesized and demonstrated as an example to investigate how B doping transforms the inertness of CNTs and turns them into an active electrocatalyst for CE of a DSSC. The main purpose of this work is to systematically explore the effect of B concentration on the electrocatalytic ability in catalyzing I_3^- ions reduction reaction and its influence on the performance of the pertinent DSSCs. The morphology, elemental configuration, defect levels, and conductivity of BCNTs with various B

doping levels were carefully examined. X-ray photoelectron spectroscopy (XPS) characterizations indicated that the B concentrations of the BCNTs were controllable from 0.40 to 3.92 at%, depending on the process conditions. The doping concentration of the BCNTs film was optimized concerning the content of B atoms with the aim of achieving the best DSSC performance. The photocurrent density-voltage characteristics of the DSSCs, using pristine CNTs, BCNTs with various B doping levels, and Pt as the CE materials were obtained at 100 mW cm^{-2} . A solar-to-electricity conversion efficiency (η) of $7.17 \pm 0.11\%$ is achieved for a DSSC with a CE containing BCNTs with 0.40 at% of B doping concentration (BCNT-0.40 at%), which is higher than that of the cell with a CE consisting of pristine carbon nanotubes (CNT, $\eta = 5.98 \pm 0.20\%$) and is comparable to that of the cell with a Pt CE ($\eta = 7.98 \pm 0.05\%$). The higher η value of the DSSC with BCNT-0.40 at% is not only attributed to the better electrocatalytic ability of its CE for the reduction of I_3^- , but also to the reduced charge transfer resistance at the CE/electrolyte interface, as could be explained by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization analysis. This work not only provides a detail report to discuss the influence of boron dopant concentrations in CNTs on the electrocatalytic ability for catalyzing I_3^- ions, but also provide a new industrial procedure to prepare highly electrocatalytic boron-doped carbon without an expensive vacuum system.

2. Experimental section

2.1. Chemicals

Poly(oxyethylene)-diamine or poly(oxypropylene-oxyethylene-oxypropylene) segmented polyether of bis(2-aminopropyl ether) (POE 2000, $M_w \sim 2000 \text{ g/mol}$) is a crystalline and water-soluble compound (waxy solid, melting point $37\text{--}40^\circ\text{C}$, amine content 0.95 meq g^{-1}) with a formula of 39 oxyethylene and 6 oxypropylene units, which was purchased from Huntsman. Tetrahydrofuran (THF, 95%) was purchased from Teida Chemicals. Lithium iodide (LiI, synthetic grade), iodine (I_2 , synthetic grade), and poly(ethylene glycol) (PEG, $M_w = 20,000$) were obtained from Merck. Monomer, 4,4'-oxydiphthalic anhydride (ODPA, 97% purified by sublimation), lithium perchlorate ($LiClO_4$), acetonitrile (ACN, 99.99%), isopropyl alcohol (IPA, 99.5%), 2-methoxyethanol ($\geq 99.5\%$), and ethanol absolute ($\geq 99.8\%$), were obtained from Sigma-Aldrich. Titanium(IV) isopropoxide (TTIP, $> 98\%$), 4-*tert*-butylpyridine (TBP, 96%), and *tert*-butanol (*t*BuOH, 99.5%) were acquired from Acros. 3-Methoxypropionitrile (MPN, 99%) was obtained from Fluka. *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium (II) bis(tetra-butylammonium) (N719 dye), 1,2-dimethyl-3-propylimidazolium iodide (DMPII) and Ti-Nanoxide HT/SP were received from Solaronix S. A., Aubonne, Switzerland. Deionized water (DI-water) with a resistivity $\geq 18.2 \text{ M}\Omega\text{-cm}$ was produced by Purelab Maxima (ELGA, UK). Boron trioxide powder (B_2O_3 , ACS reagent, $\geq 99\%$) and sodium dodecyl sulfate (SDS) were purchased from Alfa Aesar (Lancashire, United Kingdom). All the chemicals were used as received without further treatments.

2.2. Synthesis of the carbon nanotubes and boron-doped carbon nanotubes

The CNTs used as the starting material was synthesized through a water-assisted CVD. Details of the CNTs growth process were similar to that described in the literature [36,37] and can be referred to in the Supporting Information. To produce BCNT with controllable B dopant concentrations and uniform B distributions for electrochemical study, a

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