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# High performance dye-sensitized solar cell by using porous polyaniline nanotubes as counter electrode

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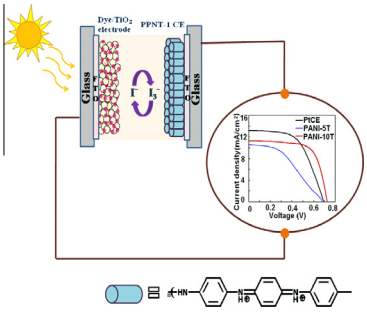
## HIGHLIGHTS

- Porous polyaniline nanotubes (PPNT-1) have been synthesized through controlled polymerization.
- A counter electrode has been designed for the low cost dye-sensitized solar cells (DSSCs).
- PPNT-1 has been employed as a substitute for platinum of counter electrode (CE).
- PPNT-1 CE achieved a high conversion efficiency of 5.57% vis-à-vis Pt CE of 5.20%.

## GRAPHICAL ABSTRACT

Porous polyaniline nanotubes have been synthesized though aqueous phase polymerization of aniline and it is employed as the counter electrode in the DSSCs showing lower charge-transfer resistance and higher electrocatalytic activity for the $I_3^-/I^-$ redox reaction than that of Pt electrode.

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## ABSTRACT

High efficiency and low cost dye-sensitized solar cells (DSSCs) have attracted much attention very recently in the context of our need for an affordable renewable energy source. Inexpensive porous polyaniline nanotubes (PPNT-1) have been synthesized through a simple method via controlled polymerization of aniline with ammonium persulfate in the presence of concentrated orthophosphoric acid. PPNT-1 has been used as a substitute for platinum to construct the counter electrode (CE) in a DSSC, which showed lower charge transfer resistance and higher electrocatalytic activity for reduction of $I_3^-$ into $I^-$ than that of Pt electrode. PPNT-1-10T CE achieved a high conversion efficiency of 5.57%, matching the performance of otherwise identical DSSCs with Pt CE (5.20%).



*Abbreviations:* DSSC, dye sensitized solar cell; CE, counter electrode; FTO, fluorine doped transparent tin oxide; PANI, polyaniline; PPNT-1, porous polyaniline nanotubes; PPNT-1-5T, porous polyaniline nanotube film prepared by 5 times spin coating; PPNT-1-10T, porous polyaniline nanotube film prepared by 10 times spin coating; FF, fill factor; HRTEM, high resolution transmission electron microscopy; BET theory, Brunauer, Emmett and Teller theory for surface area analysis; NLDFT, non-local density functional theory; XRD, X-ray diffraction.

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## 1. Introduction

Solar cells are widely acknowledged as clean energy source and this is particularly demanding to overcome the future energy crisis due to the diminishing fossil fuel [1,2]. Grätzel and his coworkers have employed $TiO_2$ nanoparticles based sensitized systems along with a series of Ru-dyes as a working electrode, a Pt counter electrode(CE), and an iodine based electrolyte system as the main components of the dye-sensitized solar cells (DSSCs) [3–5]. Recently, the high efficiency and low cost DSSCs have attracted much attention [6,7]. CE, one of the indispensable components in DSSC, is usually constructed on conducting glass substrates coated with platinum films due to its excellent electrocatalytic activity for the $I_3^-/I^-$ redox couple [8]. However, platinum as noble metal is expensive, and the cost of platinum CE is over 40% of the whole photovoltaic cell regardless of its preparation method [9]. Therefore, great effort has been made to develop low cost and more efficient cathodic materials, e.g. various carbon materials were attempted to replace Pt [10–13], but the photovoltaic conversion efficiency of the DSSC based on these carbon materials as CE was relatively low due to their poor catalytic activity. Barakat et al. have employed Pd–Co-doped carbon nanofibers with high photoactivity as counter electrodes for DSSCs [14]. However, further improvement in DSSC efficiency is not observed. In this context conducting polymers [15–20] are promising candidates for CE materials used in DSSC because of their low cost, high-conductivity, and excellent catalytic activity for $I_3^-$ reduction.

Polyaniline (PANI) is one of the most intensively studied conducting polymers during the last decade, due to its easy synthesis, high-conductivity, good environmental stability and interesting redox properties [15]. Li et al. have fabricated the microporous polyaniline thin film as counter electrode for the DSSCs [16]. Chen et al. have reported polyaniline nanofiber-carbon film as flexible counter electrodes in platinum-free dye-sensitized solar cells [17]. Zhang et al. have applied the nanostructured PANI thin film as counter electrode for DSSCs and investigated the electrochemical formation mechanism [18]. Tai et al. have prepared the highly uniform and transparent PANI counter electrodes by a facile in-situ polymerization method for the DSSCs [19]. In this context Wei et al. have fabricated phosphoric acid doped conductive polyaniline (PANI)/silica nanocomposites as supercapacitor electrodes [21]. Porosity in the nanostructured PANI could help to absorb the dye molecules at its surface making the electron transfer facile and thus can make it an efficient CE.

Herein, we report a facile synthetic route for the porous polyaniline nanotubes through simple polymerization in the presence of orthophosphoric acid and it has been successfully applied as CE for DSSCs (Scheme 1). PPNT-1 CEs exhibited good electrocatalytic activities for reduction of $I_3^-$ into $I^-$ compared to Pt CE. DSSCs using this PPNT-1-10T as CE achieved a high conversion efficiency of 5.57%, vis-à-vis that of DSSCs with Pt CE (5.20%) keeping other parameters of the cell unaltered.

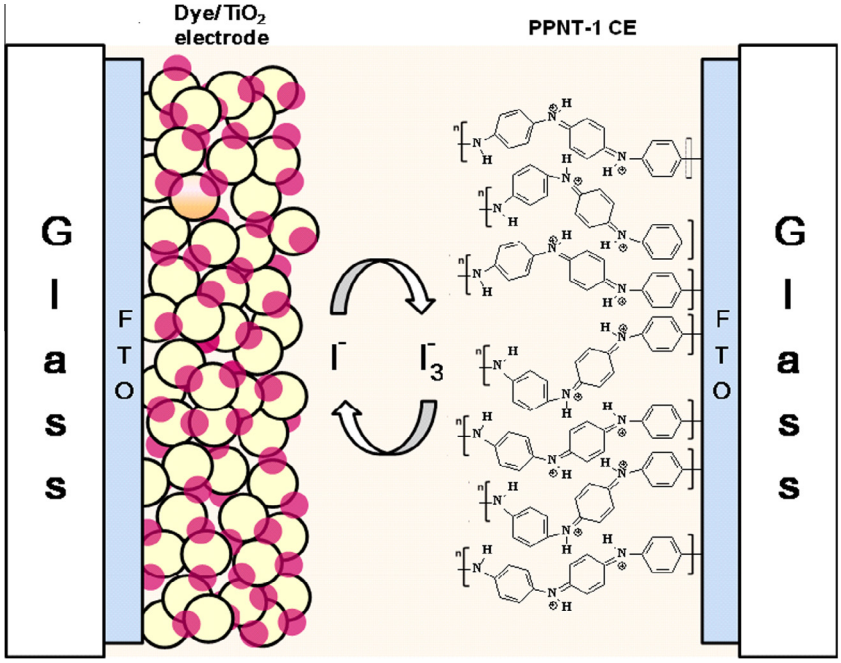
## 2. Experimental section

### 2.1. Materials

Aniline was obtained from E-Merck (AR). Ammonium persulfate $(NH_4)_2S_2O_8$, (E-Merck, GR) was used as an initiator for the polymerization in the presence of orthophosphoric acid (E-Merck, 85% pure). Lithium iodide, iodine, lithium perchlorate and chloroplatinic acid hexahydrate was procured from Sigma Aldrich. All chemicals were used without further purification.

### 2.2. Instrumentation

Nitrogen adsorption/desorption isotherms of the sample was recorded on a Quantachrome Autosorb 1C, at 77 K. Prior to the gas adsorption measurement, the sample was degassed at 373 K for 8 h under high vacuum (0.00472 mm Hg). The pore size distribution pattern of the sample was obtained by employing the non-local density functional theory (NLDFT) to the respective $N_2$ adsorption/desorption isotherm. It involves complex mathematical modeling of fluid–solid and fluid–fluid interactions along with geometrical considerations (pore geometry) and thus it provides an accurate structure of fluid confined in the pores. Powder X-ray




**Scheme 1.** Graphical representation of the polyaniline CE dye-sensitized solar cell.