



# Graphene oxide induced fabrication of pillared and double-faced polyaniline arrays with enhanced triiodide reduction capability



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## ABSTRACT

Counter electrode (CE) materials, featuring low cost, high electrical conductivity and electrocatalytic activity, are one of the key points to achieve practical application of dye-sensitized solar cells (DSSCs). To tackle with this issue, the pillared and double-faced polyaniline (PANI) nanocone arrays induced by graphene oxide (GO) (PANI/GO) are configured through *in-situ* polymerization, and the electrochemical behavior as the low-cost CE for DSSCs is revealed. The GO sheets adopted as a substrate and structure-directing agent could effectively induce the uniform and vertical growth of PANI arrays, thus producing a free and open networks. This unique structure is further capable of shortening the ionic diffusion path and providing the large contactable area to the electrolyte. And, a high power conversion efficiency of  $8.19 \pm 0.08\%$  can be achieved, being superior to those of Pt and PANI references. Moreover, the as-made PANI/GO CE also delivers an outstanding electrochemical stability. The present strategy provides a simple yet efficient method to engineer the high-efficiency and fast mass-transport catalyst for DSSCs and electrode materials for other energy storage/conversion.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs), one of the most promising alternatives to the traditional silicon-based solar cells, have triggered extensive attention in solving energy crisis due to its high energy conversion efficiency, low cost, and easy fabrication process [1–6]. The conventional DSSCs generally consist of a dye-sensitized nanocrystalline TiO<sub>2</sub> photoanode coated on fluorine doped tin oxide (FTO) glass, triiodide/iodide (I<sub>3</sub><sup>-</sup>/I<sup>-</sup>) redox electrolyte, and a counter electrode (CE) [7,8]. The CE is a key part in collecting electrons from external circuit and catalyzing the redox couple regeneration, where a steady power output can be well kept and achieved [9]. It is believed that the ideal CEs should combine these characteristics together including excellent conductivity, highly catalytic activity, and super electrochemical

stability [10–12]. Up to now, the noble metal platinum (Pt) is usually employed as an efficient CE for DSSCs [13,14]. However, the large-scale utilization of Pt CE is restricted by several drawbacks including natural scarcity, high cost, and easily corroded by iodine-based electrolytes [15–17]. In consequence, it is urgent to explore the low-cost and high efficient catalysts for the reduction of I<sub>3</sub><sup>-</sup> [18–20].

Polyaniline (PANI), featuring fascinating and controllable electrical conductivity, unique electrocatalytic activity, simple preparation process, and low cost, has also been employed as CE for DSSCs [21–24]. For example, Wu et al. prepared transparent PANI electrode through chemical deposition. The DSSCs based on this PANI CE can achieve a power conversion efficiency (PCE) of 6.7% [9]. Huang et al. employed hollow and spherical PANI particles as CE, and 6.84% of PCE is produced [22]. Wu et al. devised a bifacial DSSCs based on a transparent PANI CE. The DSSCs assembled with the bifacial transparent PANI CE deliver the PCE of 8.35% [25]. However, of the work available now, the PANI usually fails to achieve controllable preparation and assembly, thus producing a relatively tanglesome and disordered structure. Such non-

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orientated structure will restrict the mass- and electro-transport during electrocatalysis process and further lead to a relatively low catalytic activity to some degree [26].

Inspired by the analysis above, herein, a kind of hierarchical nanocomposite of pillared and oriented PANI nanocone arrays induced by graphene oxide (GO) sheets (PANI/GO) were engineered through *in-situ* polymerization. The GO adopted was used as the substrate and structure-directing agent to induce the nucleation and assembly of PANI nanocone arrays. The abundant oxygen-containing function groups on the GO surface would act as the anchoring sites for inducing nucleation and growth of the PANI seeds. The pillared and double-faced PANI nanocone arrays on GO sheets also function as a scaffold, which effectively prevents the self-agglomeration of GO. Benefiting from these characteristics, the as-made PANI/GO features an interconnected and open structure, further accelerating the mass transfer and exposing more active sites that are required during electrocatalytic process. When employing the PANI/GO composite as CE, the corresponding DSSCs show a remarkable conversion efficiency of  $8.19 \pm 0.08\%$ , which is superior to  $7.37 \pm 0.09\%$  of Pt CE and  $7.59 \pm 0.12\%$  of pure PANI CE.

## 2. Experimental section

### 2.1. Synthesis of GO

The GO used here was prepared by the modified Hummer's method that has been reported before [27–29]. For a typical run, firstly, graphite powder (5 g) and sodium nitrate (1.5 g) were added into a beaker (1 L) containing 130 mL of concentrated sulfur acid (98%), and stirred at 0 °C in an ice-bath for 2 h. Then, 15 g of potassium permanganate was carefully added, and another 2 h was needed to stir. After stirring evenly, the beaker was transferred to a constant temperature water bath of 35 °C and kept for stirring for 1 h. Thereafter, 230 mL of deionized water was dropwise added into the mixture and kept at 98 °C for 30 min. Additional 400 mL of deionized water and 10 mL of hydrogen peroxide were poured into the solution. Finally, the product was centrifuged and washed by deionized water repeatedly until the pH changed from acidity to neutral, then the GO dispersion was produced.

### 2.2. Preparation of PANI and PANI/GO array composites

PANI/GO composites were fabricated by *in-situ* polymerization of aniline in the presence of GO. The mass ratio of GO to aniline was 8% and 10%, respectively, of which the addition amount of GO is constant. 10 mg of GO was added into 20 mL of 1 M HClO<sub>4</sub> aqueous solution and ultrasonicated by sonifier cell disrupter for 30 min. Afterward, a certain amount of aniline monomer was dropped into the previous mixture and stirred for 30 min at –10 °C. In order to prevent to be frozen at the reaction solution, 5 mL of alcohol was added during the stirring process. A certain amount of ammonium persulfate (APS, the molar ratio of aniline to APS is 1.5) was added into the reaction system and the mixture was kept stirring at –10 °C for 24 h to accomplish full *in-situ* polymerization process. After being collected by filtrating through polytetrafluoroethylene membrane (0.45 μm) and washed with 0.1 M HClO<sub>4</sub> and ethanol, the product was dried for 24 h in a vacuum freeze drying. For comparison, the PANI/GO composites that were produced at different polymerization time and pure PANI were synthesized following the same procedure.

### 2.3. Fabrication of various CEs

The as-made samples such as GO, PANI, PANI/GO were mixed with Poly(vinylidene fluoride) by the mass ratio of 9:1 and added a

few drops of N-methyl-2-pyrrolidone into the mixture, respectively. Then, the mixture was ground until the uniform slurries were got. The as-obtained slurries were transferred onto the fluorine-doped tin oxide (FTO) glasses using doctor-blade method, and followed by drying in vacuum at 90 °C for 5 h, yielding different CEs.

### 2.4. Assembly of DSSCs

The TiO<sub>2</sub> photoanodes (Yingkou OPE Tech New Energy Co., Ltd., China) were heated to 500 °C for 30 min and cooled to 100 °C later on [30]. Then the TiO<sub>2</sub> films were immersed in an ethanol solution composed of 0.5 mM N719 dye (Yingkou OPE Tech New Energy Co., Ltd., China) for 24 h, following by rinsing with ethanol to wash out redundant dye attached on the surface and drying with air flow. The dye-loaded TiO<sub>2</sub> photoanodes and the as-made CEs with the redox electrolyte (OPV-AN-I, Yingkou OPV Tech New Energy Co., Ltd., China) were assembled together into the DSSCs. The two electrodes were separated by hot-melt Surlyn film (Surlyn, Yingkou OPV Tech New Energy Co., Ltd., China) with 45 μm thickness and sealed through hot-pressing. The sealed cells with an active area of 0.16 cm<sup>2</sup> were used for photocurrent-voltage test.

### 2.5. Characterization

The surface morphologies of GO, PANI, and PANI/GO were examined using field-emission scanning electron microscopy (FESEM, Nova NanoSEM 450) and transmission electron microscopy (TEM, Tecnai F30). X-ray diffraction patterns were recorded on an X-ray diffractometer (D/Max 2400, RIGAKU, Japan) with Cu K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). Raman spectra of all samples were obtained by a DXR Raman Microscope (Thermo Scientific) with an excitation wavelength of 532 nm. The Fourier Transform Infrared Spectroscopy (FTIR) was recorded with a Fourier transform infrared spectrometer (Thermo Scientific, 6700). Cyclic voltammetry (CV) was measured by a three-electrode system in the supporting electrolyte consisting of 0.1 M LiClO<sub>4</sub>, 10 mM LiI, and 1 mM I<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>, in which the Ag/Ag<sup>+</sup> electrode was used as the reference electrode, the Pt wire as the CE, and the as-prepared CE was taken as the working electrode. The electrochemical impedance spectroscopy (EIS) and the Tafel polarization curves were measured using dummy cells assembled by two identical CEs through Multichannel Potentiostats (VSP, Bio-Logic, France). The photocurrent density-voltage (*J-V*) curves were examined by a Keithley 2400 source meter equipped with a AAA solar simulator (94032A, Newport, US) under AM 1.5 G and 100 mW cm<sup>-2</sup>.

## 3. Results and discussion

### 3.1. Synthesis and structural characterization

The fabrication process of GO-induced PANI nanocone arrays is illustrated in Fig. 1. In the absence of GO, the aniline monomer tends to make free nucleation and growth, which leads to the tanglesome and disordered PANI structure (process I). GO is usually inclined to make self-aggregation and restack due to the large specific surface area and interface energy (process II). Interestingly, when combining GO with aniline monomer, the PANI nanocone arrays can grow and assemble vertically on GO surface (process III). During this nucleation and growth process, the PANI is coated on the surface of GO firstly. Then the nanoparticles or clusters of PANI form and are gradually transformed into nanocones as an increase of polymerization time, evidenced by the SEM images of PANI/GO composites that were produced at different polymerization time (Fig. S1). Thereinto, GO with abundant oxygen-containing

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