



Serrated, flexible and ultrathin polyaniline nanoribbons: An efficient counter electrode for the dye-sensitized solar cell



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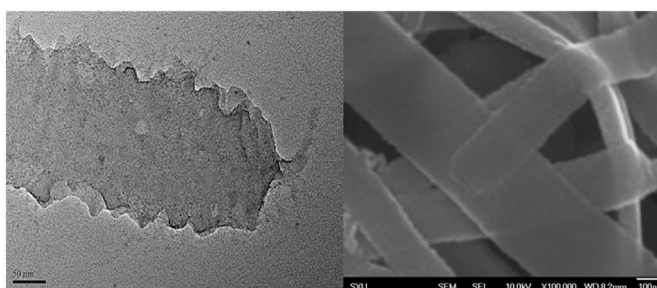
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HIGHLIGHTS

- Serrated, flexible and ultrathin PANI NRs are successfully prepared.
- PANI NRs CE shows plenty of catalytic active sites and fast electron transport.
- Pt-free DSSC based on the PANI NRs CE reaches 7.23% of the efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Development of cost-effective counter electrodes (CEs) and enhancement of power conversion efficiency are two persistent objectives for dye-sensitized solar cells (DSSCs). We report a novel method for synthesizing the state of art polyaniline nanoribbons (PANI NRs) CE with serrated, flexible and ultrathin nanostructure by *in situ* polymerization of aniline on an inorganic template, followed by acid etching. Herein, electrospun vanadium pentoxide (V_2O_5) nanofibers are chosen as templates to deposit PANI by a chemical bath polymerization method, which are served as the oxidants as well. Owing to its abundant active sites and the good contact performance, the PANI NRs CE shows high catalytic activity and the DSSC based on the PANI-c NRs CE shows a photoelectric conversion efficiency of 7.23% under full sunlight illumination (100 mW cm^{-2} , AM 1.5 G), which is 97.44% that of the Pt-based DSSC (7.42%). Therefore, the high performance of PANI NRs can be considered as a cost-effective CE for the DSSC.

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1. Introduction

Increasing energy demands and environmental pollution problems have prompted research on clean and renewable energy sources. Utilization of solar energy has been demonstrated to be highly promising. Dye-sensitized solar cell (DSSC) has currently attracted widespread academic and commercial interests because

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of its low cost, high efficiency, and eco-friendly fabrication process, since its first prototype was reported in 1991 by O'Regan and Grätzel [1–4]. In general, a DSSC consists of three important parts: a dye-sensitized titanium dioxide (TiO_2) as the photoanode, an iodine based electrolyte, and a counter electrode (CE). Due to its high conductivity and catalytic activity for the reduction of triiodide (I_3^-) to iodide (I^-), the platinum (Pt) CE is widely used in the DSSC [5]. However, Pt is expensive and the cost of Pt CE is over 40% of the whole DSSC, regardless of its preparation method [6,7]. Meanwhile, Pt could be dissolved in I^-/I_3^- redox couple electrolyte to produce PtI_4 [8]. These defects directly limit the commercial application and the long term stability of the DSSC [8,9]. Several substitute materials, such as transition metal compounds [10–15], conducting polymers [16–18], carbon materials [19–21], and metal alloys [7,22] have been widely investigated to replace Pt, or at least, to reduce the cost for the preparation of CEs.

As a representative conducting polymer, polyaniline (PANI) is suitable for the DSSC CE due to its superior catalytic activity for I_3^- reduction and environmental stability [23,24]. Xiao et al. fabricated PANI nanofibers CE with a short-branched structure by employing two-step cyclic voltammetry approach and the DSSC assembled with this CE exhibited an enhanced efficiency of 6.21% [18]. Lee et al. reported a novel method to synthesize highly porous nanostructured PANI CE using carbon nanodots as a nucleating agent and exhibit a superior power conversion efficiency of 7.45% [25]. Recently, the applications about the state of art PANI nanoribbons (PANI NRs) are becoming more and more popular in foldable supercapacitors [26,27]. However, very few studies have been investigated using PANI NRs as the CE in DSSCs.

Vanadium pentoxide nanofibers (V_2O_5 NFs) usually fabricated by an electrospinning method are widely used as templates to prepare conducting polymer NFs, such as pyrrole NFs [28,29]. However, the electrospinning precursor they used, vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$), whose sublimation temperature begins at 140 °C [30], is easy to be lost before converting to V_2O_5 NFs template during the calcination process. Moreover, the uses of organic solvents for the electrospun have also led to high cost and great environmental pollution.

In this study, we chose ammonium metavanadate (NH_4VO_3) as the V_2O_5 source to increase the yield of V_2O_5 NFs, which was dissolved in poly(vinyl alcohol) aqueous solution for the electrospun. The as-prepared V_2O_5 NFs acted as both oxidant and sacrificial template to synthesis PANI NRs via a simple chemical bath polymerization method, subsequent acid etching technique and drying treatment. Scheme 1 shows the preparation processes of the PANI NRs CE. Owing to the serrated structure on the edge and surface of PANI NRs provided plenty of catalytic activity sites, and the flexible and ultrathin structures enhanced the contact performance among the PANI NRs and FTO substrate, the PANI NRs CE promoted the efficiency of catalyzing I_3^- reduction and charge transmission. The DSSCs assembled with the PANI NRs CE exhibited an enhanced photovoltaic conversion efficiency of 7.23%, which was 97.44% that of the Pt-based DSSC (7.42%).

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, $M_w = 78,000$), ammonium metavanadate (NH_4VO_3), and aniline (ANI, 98%) were purchased from Sigma-Aldrich. Methanol, hydrochloric acid (HCl), iodine, lithium iodide, lithium perchlorate, tetrabutyl ammonium iodide, 4-*tert*-butylpyridine, guanidine thiocyanate, and acetonitrile were purchased from Shanghai Chemical Agent Ltd., China (Analysis purity grade). Dye N719 was purchased from Dyesol, Australia. The above

agents were used without further purification. F-doped tin oxide (FTO) glass substrates were purchased from NSG, Japan ($15 \Omega \text{ sq}^{-1}$).

2.2. Preparation of PANI NRs CE

Firstly, the V_2O_5 nanofibers (V_2O_5 NFs) were prepared through electrospinning technique according to the previous report [31]. In brief, 80 mg PVA was firstly dissolved in 1.0 mL deionized water and heating at 80 °C with vigorous stirring for 5 h. Then 20 mg NH_4VO_3 was added to the above PVA solution. After the mixture was stirred at 80 °C for 3 h, a viscous light-yellow clear solution of PVA- NH_4VO_3 was obtained for the electrospun. The electrospun mixture was supplied with a rate of about 1.0 mL h^{-1} by a stainless-steel syringe pipette needle carrying a potential of +20.0 kV. PVA- NH_4VO_3 fibers were collected on a sheet of electrically grounded aluminum foil placed 14 cm below the syringe tip. The as-prepared fibrous film was peeled off from the collector and cut into a small pieces, and then pasted onto the humid FTO substrate (1.5 cm \times 2 cm), then annealed in air atmosphere at 450 °C for 0.5 h to obtain V_2O_5 NFs.

Secondly, chemical bath polymerization process was conducted to prepare the V_2O_5 -PANI NFs based on different concentration of ANI solutions. In a typical procedure, V_2O_5 NFs substrates were soaked in five beakers, in which containing 0.10 M HCl and ANI with different concentrations of 0.60 M, 0.70 M, 0.80 M, 0.90 M, and 1.00 M in methanol, respectively, for 24 h to obtain the V_2O_5 -PANI NFs.

Finally, removing the residual V_2O_5 template (by etching in 1.00 M HCl solution overnight), the PANI nanotubes (PANI NTs) were obtained. After a drying process at 60 °C for 30 min, the PANI NTs shrink gradually and finally forming the PANI nanoribbons (PANI NRs), which were defined as PANI-a, PANI-b, PANI-c, PANI-d, and PANI-e NRs, respectively.

For comparison, the PANI bulk-like CE was also fabricated. The as-prepared viscous light-yellow clear solution of PVA- NH_4VO_3 was directly dropped on the FTO surface and then annealed at 450 °C for 30 min to get the V_2O_5 nanoparticles (V_2O_5 NPs) template. Then the chemical bath polymerization process was conducted to prepare the V_2O_5 -PANI NPs based on ANI solutions with the concentration of 0.80 M and then above-mentioned acid etching and drying processes were carried out to obtain the PANI bulk-like CE. Moreover, a thermal decomposition Pt CE was also employed, which was prepared by dipping H_2PtCl_6 isopropanol solution with a concentration of 0.50 wt% onto the surface of the FTO glass, and then heated at 450 °C for 30 min.

2.3. Preparation of TiO_2 anode

The mesoporous TiO_2 anode was fabricated according to our previous works [4,7,18]. The mesoporous TiO_2 anode based on as-prepared TiO_2 colloid was coated on the FTO substrate by a doctor-scraping technique. The thickness of the TiO_2 film was about 3.7 μm (Fig. S1), which was controlled by the thickness of the adhesive type around the edge of the FTO substrate. After drying at 20 °C, the TiO_2 anode was sintered in a muffle furnace at 450 °C for 30 min. The resultant mesoporous TiO_2 anode was immersed in a 2.5×10^{-4} M solution of dye N719 in absolute ethanol solution for 24 h to adsorb the dye adequately.

2.4. Assembly of DSSCs

The DSSC was assembled by injecting the redox electrolyte into the gap between the TiO_2 anode and a PANI CE. The two electrodes were clipped together and constituted the whole cell with a sandwich structure. The redox electrolyte composed of 0.60 M tetrabutyl ammonium iodide, 0.10 M lithium iodide, 0.10 M iodine,

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