

# Graphene modified vanadium pentoxide nanobelts as an efficient counter electrode for dye-sensitized solar cells



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## ABSTRACT

Efficient dye-sensitized solar cells (DSSCs) were fabricated using graphene modified vanadium pentoxide nanobelts (GVNBs) as a cost-effective counter electrodes (CEs). GVNBs were synthesized by facile one-step hydrothermal method without using any reducing agent and harmful solvents. These novel nanocomposite have been tested as a counter electrode in DSSCs for the first time, which showed high solar to electrical energy conversion efficiency. The GVNBs showed the excellent electrocatalytic activity for the reduction of triiodide to iodide due to the synergetic effect between one-dimensional shape of vanadium pentoxide nanobelts and reduced graphene oxide. The DSSCs based on the GVNBs CEs have reached a high power conversion efficiency of 6.17%, which is comparable to that (7.98%) of the conventional platinum (Pt)-based CEs. This result indicate that GVNBs can be used as an alternative to conventional Pt-based CEs for the highly efficient DSSCs.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) are one of the promising alternatives to conventional silicon solar cells, which have attracted many researchers due to their variety of colors, low cost, facile fabrication method, and high power conversion efficiency (PCE) [1–6]. In general, very simple structure with a photo anode (dye-sensitized TiO<sub>2</sub> nanocrystalline film), an electrolyte (I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple), and a counter electrode (platinized conductive glass) has been adopted for their fabrication process [7,8]. Platinum (Pt) is generally used as a counter electrode (CE) material for catalytic reduction of I<sub>3</sub><sup>-</sup> to I<sup>-</sup> in DSSCs because of the following advantages such as superior electrocatalytic activity, conductivity and excellent stability in iodine based liquid electrolyte. However, Pt is a low abundant and one of the most expensive components of DSSCs, which may hinder the commercialization of DSSCs to wide spread of consumers [9]. To overcome this problem, variety of low cost materials, such as carbonaceous materials, inorganic compounds,

conductive polymers and their composite have been reported as an alternative CE to Pt in DSSCs [10–13]. Among these catalysts, nanostructured vanadium oxide is one of the candidates as catalyst. For instance, Wu et al. have demonstrated that vanadium (III) oxide (V<sub>2</sub>O<sub>3</sub>) was used as CE in common liquid type DSSCs with 5.4% of PCE [14]. However, improvement of PCE in device is inevitable towards commercialization. In recent years, considerable studies have been devoted to make it better for electrical conductivity of metal compounds by conductive carbon modification [15–17]. Among the carbon derivatives, graphene, a single sheet of carbon atoms in the form of a two-dimensional honeycomb configuration is considered as the promising materials nowadays due to its high conductivity, superior charge transport mobility, mechanical flexibility, and large surface area [18,19]. Metal compounds with graphene modification for high performance in DSSCs were carried out recently. For example, Bajpai et al. have attempted to fabricate CEs using NiO/graphene mixture by the drop casting of graphene solution, followed by pulsed laser deposition of NiO nanoparticles [20]. Li et al. have synthesized NiS<sub>2</sub>/reduced graphene oxide (rGO) nanocomposite for efficient DSSCs [21]. Both composite materials showed higher performance than those of the individual components due to the synergetic effect between metal compounds and graphene sheets.

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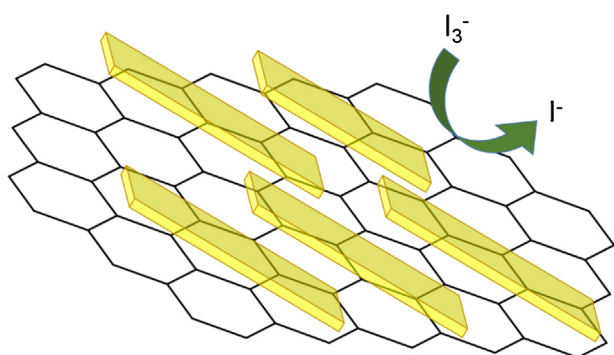


Fig. 1. Schematic image of GVNBs for counter electrode in DSSCs.

Meanwhile, graphene decorated  $V_2O_5$  nanobelts (VNBs) have been synthesized by simple mixing of commercial  $V_2O_5$  particle (VO) with GO at room temperature without using any detrimental oxidizing or reducing chemical agents and surfactants in our previous work [22]. However, this method has taken a long time to fabricate one-dimensional (1-D) shape ( $V_2O_5$ /graphene) composite materials. To synthesize graphene decorated VNBs (GVNBs) rapidly, we have attempted to fabricate composite using facile approach via one-step hydrothermal process by mixing VO with graphene oxide (GO) in D.I., which finally yield 1-D graphene modified  $V_2O_5$  nanobelts [23]. Various functional groups at the surface of the GO leads to the formation of 1-D shape  $V_2O_5$  nanobelts from commercial  $V_2O_5$  nanoparticles, while GO was reduced into rGO simultaneously without using any kinds of the reducing agent and harmful solvents too. In this work, the as synthesized materials have been demonstrated for the first time to utilize it as a CE catalysts in DSSCs, which showed enhanced PCE value as compared to that prepared from conventional Pt. The catalytic activity of various counter electrodes has also been analyzed using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV). The enhanced performance of the GVNBs CE could be ascribed to the efficient charge polarization, since 1-D nanobelts have more favorable to electron transport than that of the sphere shape  $V_2O_5$  nanoparticles. Further graphene modified GVNBs showed better charge transfer property and low sheet resistance when compared to the pure VNBs. Moreover, the PCE value of DSSCs made of GVNBs CE (6.17%) is comparable to that of the conventional Pt based DSSCs (7.98%) under AM 1.5 G simulated solar light ( $100 \text{ mW cm}^{-2}$ ). Therefore, the GVNBs can be a viable alternative to conventional Pt-based CEs.

## 2. Experimental section

### 2.1. Synthesis of graphene oxide (GO) and partially reduced graphene oxide (prGO)

The GO was prepared according to the modified Hummer's method, as reported in literature [24]. 10 g of  $K_2S_2O_8$ , and 10 g of  $P_2O_5$  were added into the 50 mL of conc.  $H_2SO_4$  solution at  $80^\circ\text{C}$ . 12 g graphite powder put into the above solution and then kept for 4.5 h at the same temperature. The mixture was diluted with 2 L of deionized (DI) water and left overnight. After washing with DI water, the suspension was dried under ambient conditions. Pre-oxidized graphite was added to 460 mL of  $H_2SO_4$  on ice bath at  $0^\circ\text{C}$ , and 60 g of  $KMnO_4$  (Sigma–Aldrich,  $\geq 99.0\%$ ) was then slowly added to the suspension under stirring below  $10^\circ\text{C}$  for further oxidizing. This mixture was kept stirring for 2 h at about  $35^\circ\text{C}$ . Adding 920 mL of DI water, and then a 2.8 L of DI water, 50 mL of 30%  $H_2O_2$  (SAMCHUN pure chemical) was added to the resultant followed by this mixture was centrifuged and washed with HCl and DI water. And the suspension then was purified by dialysis for 2 weeks. Finally, GO sheets are prepared via drying process at  $50^\circ\text{C}$  for 3 days. Partially reduced rGO (prGO) was prepared by facile hydrothermal reaction [25,26]. 0.5 g of GO was dispersed in 40 mL of DI water, and then sonicated for half an hour, which was transferred to teflon-lined stainless steel autoclave and kept at  $180^\circ\text{C}$  for 48 h. The final product was washed with distilled water and then freeze-dried ( $-95^\circ\text{C}$ , 5 mTorr) for 72 h.

### 2.2. Synthesis of vanadium pentoxide nanobelts (VNBs)

VNBs were synthesized by a simple hydrothermal route as follows. First, 0.364 g of commercial  $V_2O_5$  particle (VO) was dispersed in the 30 mL of DI water, then 5 mL of 30%  $H_2O_2$  was added to the suspension and stirred for 1 h. This solution was shifted to the 50 mL stainless autoclave with a teflon line, which was kept in furnace at  $180^\circ\text{C}$  for 48 h. The resulting precipitate was washed with DI water and then freeze dried ( $-95^\circ\text{C}$ , 5 mTorr) for 72 h.

### 2.3. Synthesis of graphene decorated vanadium pentoxide nanobelts (GVNBs)

GVNBs were synthesized as follows. 0.3 g of VO and as synthesized 0.03 g (10 wt% of VO) GO have been added into 20 mL of DI water, respectively. GO solution was sonicated for 1 h and then put into the VO suspension followed by stirring at room temperature for 2 h. The obtained slurry was shifted to 50 mL

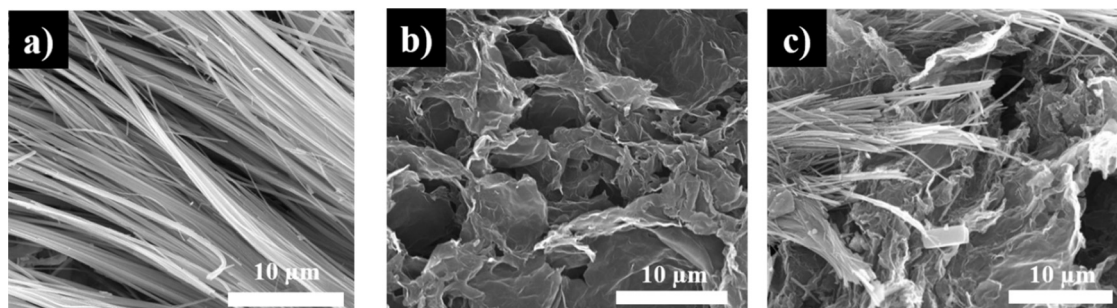


Fig. 2. SEM images of the (a) VNBs, (b) prGO, and (c) GVNBs synthesized by the hydrothermal reaction.

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