



# Tungsten oxide nanowires grown on graphene oxide sheets as high-performance electrochromic material



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## ABSTRACT

In this work, we report the synthesis of a novel hybrid electrochromic composite through nucleation and growth of ultrathin tungsten oxide nanowires on graphene oxide sheets using a facile solvothermal route. The competition between the growth of tungsten oxide nanowires and the reduction of graphene oxide sheets leads to the formation of sandwich-structured tungsten oxide-reduced graphene oxide composite. Due to the strongly coupled effect between the ultrathin tungsten oxide nanowires and the reduced graphene oxide nanosheets, the novel electrochromic composite exhibited high-quality electrochromic performance with fast color-switching speed, good cyclic stability, and high coloration efficiency. The present tungsten oxide-reduced graphene oxide composite represents a new approach to prepare other inorganic-reduced graphene oxide hybrid materials for electrochemical applications.

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## 1. Introduction

In the past few years, electrochromic (EC) materials, which are capable of changing their optical properties reversibly or persistently under an external electrical voltage, have attracted tremendous attention due to their potential applications in energy-saving smart windows, high contrast displays, sunroofs, and antiglare mirrors [1–3]. Especially, EC smart windows represent a green environmental technology to cope the energy crisis because they can effectively save energy by adjusting sun heat with low energy consumption [4,5].

As **one important type** of the functional oxide semiconductors, tungsten oxides are the most promising EC materials due to their easy preparation, fast color-switching speed, high coloration efficiency, and ideal cyclic stability [6]. With the rapid development of nanoscience and nanotechnology, considerable effort has been recently devoted to one-dimensional (1D) tungsten oxide nanomaterials (WONMs), which exhibit enhanced EC properties compared with their bulk counterpart form due to their large surface-to-volume ratio, open structures, and short diffusion distance of ions. Till now, a series of 1D tungsten oxide nanostructures as electrochromic materials have been prepared, such as WO<sub>3</sub> nanowires/nanorods [7,8], WO<sub>3</sub> nanowire arrays [9], WO<sub>3</sub>

nanoplates [10], W<sub>18</sub>O<sub>49</sub> nanowires [11], W<sub>18</sub>O<sub>49</sub> mesocrystals formed by ultra-thin nanowires [12], W<sub>18</sub>O<sub>49</sub> nanobundles [13], W<sub>18</sub>O<sub>49</sub> nanoflowers [14], etc. For the practical EC application, the 1D WONMs need to be re-constructed as EC films on conductive substrates. During the preparation of EC films, however, the 1D WONMs prefer to aggregate or stack and form large structures, which would reduce their interfacial contact area with the electrolyte and hinder the ion diffusion in the EC films. Therefore, it is still challenge to take full advantages of the 1D WONMs as EC materials.

Recently, graphene and its derivatives such as graphene oxide (GO) and chemically reduced graphene oxide (RGO) have emerged as **new promising platforms** for the design of a diversity of electronic devices [15,16]. In particular, the GO sheets, which possess many oxygenated functional groups, provide chemically reactive sites for anchoring functional inorganic oxide semiconductors [17,18]. Under well controlled synthetic conditions, the oxide semiconductors can be strongly coupled with the GO sheets to form novel hybrid composite, while the GO sheets can be simultaneously reduced to RGO sheets [19]. In addition, the interaction between the inorganic precursors and the GO supports could realize *in situ* growth of low-dimensional oxide semiconductor nanostructures on the GO sheets with controllable morphology, size, structure, dispersion, and coverage density [20,21]. In spite of lower electrical conductivity and slower carrier mobility than graphene, the RGO sheets could also significantly enhance functionalities of the inorganic oxide semiconductors. Up to now, the RGO sheets have been

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widely composited with diverse oxide semiconductors and they have found many potential applications in supercapacitors [22], solar cells [23], photocatalysis [24], and Li ion battery [25]. Since the EC performance depends strongly on the diffusion of ions in the EC materials [26]. Due to the large specific surface area, open 2D permeable channels, a certain degree of electrical conductivity, and the ability to anchor other inorganic materials, the RGO sheets would certainly facilitate the ion diffusion and accelerate the charge transfer in the EC device [27,28]. Therefore, it can be predicted that, the distinctive EC performance of the 1D WONWs could be strengthened through the incorporation with the RGO sheets.

In the present study, we report the synthesis of a novel tungsten oxide nanowires-reduced graphene oxide (WONWS-RGO) composite with GO sheets as supports through a facile solvothermal route as well as its promising EC performance. The WONWS-RGO composite are composed of sandwich-like sheets of ultrathin WONWs *in situ* grown on the RGO supports, which have been found to exhibit high-quality electrochromic performance with fast color-switching speed, good cyclic stability, and high coloration efficiency.

## 2. Experimental

### 2.1. Chemical Materials

Potassium permanganate ( $\text{KMnO}_4$ ), concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ , 98%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), tungsten hexachloride ( $\text{WCl}_6$ ), ethanol, and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade. ITO-coated glass was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.

### 2.2. Preparation of GO sheets

The modified pressurized oxidation method was employed to prepared the GO sheets with powdered flake graphite as raw materials [29]. Typically, 0.5 g of graphite and 3 g of  $\text{KMnO}_4$  were firstly put into a Teflon-lined reaction vessel of 50 ml capacity. 30 ml of  $\text{H}_2\text{SO}_4$  (98%) was added to the vessel. The reaction vessel was sealed in a stainless steel autoclave, which was kept at  $0^\circ\text{C}$  in a refrigerator for 1.5 h and then heated at  $100^\circ\text{C}$  in a Muffle furnace for 2 h. After natural cooling to room temperature, the as-synthesized product was diluted with distilled water under mechanical stirring. Then,  $\text{H}_2\text{O}_2$  was slowly added until an earth yellow suspension occurred. Finally, the GO suspension was filtered, washed by distilled water, and centrifuged for collection.

### 2.3. Preparation of WONWS-RGO composite

The tungsten oxide nanowires-reduced GO (WONWS-RGO) composite was synthesized by a solvothermal route using the as-prepared GO sheets as **supports**, tungsten hexachloride as precursor, and ethanol as solvent, as similar to our previous work [30]. In a typical synthesis, 5 mg of GO sheets and 50 mg of  $\text{WCl}_6$  were dissolved in 30 ml of ethanol to obtain a solution, which **was** subsequently transferred into a Teflon-lined high-pressure reaction vessel of 50 mL capacity. The reaction vessel was sealed and heated at  $200^\circ\text{C}$  in a Muffle furnace for 8 h. After the reaction, the vessel was taken out of the furnace and naturally cooled down to room temperature. Finally, the as-synthesized products **were** washed thoroughly with distilled water several times, and centrifuged with ethanol and acetone for further examination.

### 2.4. Characterization

The crystalline structure of the as-prepared products **was** characterized by X-ray diffractometer (XRD, D/MAX-2500, Cu radiation,  $\lambda=1.540598\text{ \AA}$ ). The  $2\theta$  range was  $5\text{--}80^\circ$  with a step of  $0.013^\circ$  and a scanning rate of  $10^\circ\cdot\text{min}^{-1}$ . The morphology of the as-prepared products was analyzed by **using** a high resolution transmission electron microscope (HRTEM, JSM 2100F, operated at 200 kV). Raman spectra were acquired from a Senterra R200-L Raman microscope, using a diode laser with excitation at 532 nm

### 2.5. EC measurement

The EC films of the WONWS-RGO composite were fabricated by ways of wire rod printing [31]. The  $\text{W}_{18}\text{O}_{49}$  NWs-rGO composite **was** firstly dispersed in ethanol to form a suspension, which **was** dropped onto transparent ITO coated glass with dimensions of  $20\text{ mm} \times 20\text{ mm} \times 0.5\text{ mm}$ . Then, a rod was rolled over the solution, leaving uniform, thin EC films on the ITO substrate. The EC films were dried under irradiation of high brightness light provided by a 1000 W filament lamp to prevent agglomeration. Electrochromic properties of the WONWS-RGO EC films were measured in a propylene carbonate solution of 0.5 M  $\text{LiClO}_4$  by using Autolab Potentiostat (PGSTAT 302 N). Pt foil was used as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammetric (CV) curves of the WONWS-RGO EC **films** were recorded at varied scanning rates. Chronoamperometry (CA) tests were conducted under a square-waved potential of  $\pm 2.0\text{ V}$ , 30 s for each state. **The optical transmittance spectra of the WONWS-RGO EC films were recorded using a UV-vis spectrometer (Lambda 35).**

## 3. Results and Discussions

Fig. 1a shows the XRD patterns of the GO sheets and the WONWS-RGO composite. The (001) reflection **possesses** the most intense diffraction peak at  $10.2^\circ$ , which is in good agreement with typical GO [32]. The increased interlayer spacing (0.79 nm) proves the effective oxidation of graphite [33]. The dominant peaks (010) and (020) of the XRD pattern of the WONWS-RGO composite were attributed to monoclinic  $\text{W}_{18}\text{O}_{49}$  (JCPDS 71-2450), indicating the successful formation of  $\text{W}_{18}\text{O}_{49}$  [34–36]. The disappearance of the (001) diffraction peak evidences both the exfoliation of the regular stack of layered GO sheets and the reduction of GO to RGO after the solvothermal process.

The Raman spectra further identify the structural features of the GO sheets and the WONWS-RGO composite, as shown in Fig. 1b. The G and 2D peaks are related to the  $\text{sp}^2$  hybridized C–C bonds, while the D peak is characteristic of the structural defects [37–39]. The Raman spectrum of GO sheets shows the D band at  $1342\text{ cm}^{-1}$  and the G band at  $1582\text{ cm}^{-1}$ . For the WONWS-RGO composite, there is no obvious change in the peak location, suggesting that the structure of GO was maintained after the coupling of tungsten oxide and GO sheets. Notably, the D–G ratios increases from 0.86 for the GO sheets to 1.14 for the WONWS-RGO composite, suggesting the chemical reduction of GO to rGO [40]. The Raman spectra of the WONWS-RGO composite shows distinct 2D peak at  $2686\text{ cm}^{-1}$ , indicating better graphitization compared to the GO sheets. The broader 2D peak also indicates that there are few-layer RGO sheets in the WONWS-RGO composite [41].

Fig. 2a shows the TEM image of the multilayered GO sheets, which consist of thin stacked platelets with evident long-range fold and have well-defined few layered structure at the edges. With the GO sheets as **supports**, ultralong and ultrathin WONWs were efficiently synthesized through the simple solvothermal process, accompanied by the reduction of GO to RGO. As seen from Fig. 2b,

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