



# Electrochemical fabrication of interconnected tungsten bronze nanosheets for high performance supercapacitor

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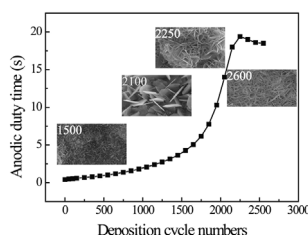
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## HIGHLIGHTS

- Fabrication of interconnected tungsten oxide nanosheets by PLPG method.
- Hierarchical electrode construction by oxide nanosheets grown on Ex-GF.
- The obtained  $\text{WO}_3/\text{Ex-GF}$  electrode displays high capacitance of  $5.95 \text{ F cm}^{-2}$ .
- 60% capacitance retention for  $\text{WO}_3/\text{Ex-GF}$  upon 50 times current increase.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Interconnected  $\text{H}_{0.12}\text{WO}_3 \cdot \text{H}_2\text{O}$  nanosheets with high electrochemical performances are fabricated on partial exfoliated graphite substrate (Ex-GF) by potential-limited pulse galvanostatic method (PLPG). The dead volume problem of bulk pseudocapacitive materials is addressed by the novel interconnected nanosheets structure, enabling a large specific capacitance of  $5.95 \text{ F cm}^{-2}$  ( $495.8 \text{ F g}^{-1}$ ) at  $2 \text{ mA cm}^{-2}$ . Merited from the fluent electrolyte penetration channels established by the plenty voids among nanosheets, as well as fast electron transportation in the electronic conductive tungsten bronze which is directly grown from graphite substrate, the obtained  $\text{WO}_3/\text{Ex-GF}$  demonstrates excellent rate capability. The material can maintain 60.0% of its capacitance when the discharge current density increases from 2 to  $100 \text{ mA cm}^{-2}$ . Moreover,  $\text{WO}_3/\text{Ex-GF}$  doesn't show capacitance decay after 5000 galvanostatic charge-discharge cycles, displaying its super stability. Furthermore, a high performance asymmetric supercapacitor assembled by using  $\text{WO}_3/\text{Ex-GF}$  and electrochemically fabricated  $\text{MnO}_2/\text{Ex-GF}$  as negative and positive electrodes, respectively displays a high energy density of  $2.88 \text{ mWh cm}^{-3}$  at the power density of  $11.1 \text{ mW cm}^{-3}$ , demonstrating its potential application for energy storage.

## 1. Introduction

Tungsten oxides are attractive electrode materials for pseudocapacitors as electrochemical exchanges among their multiple oxidation states are intrinsically fast and reversible due to the similar W-O bond length, so they are available to store charge in a wide range of potential windows [1]. Thus tungsten oxides are good candidates of negative electrode materials for asymmetric supercapacitors to significantly increase the operating voltage for energy density enhancement [2–4]. However, capacitance contributions of most of the tungsten oxides are

limited due to the restricted electrochemical reaction in the bulk oxides [1]. Nanostructure fabrication of tungsten oxides and their composites is a good way to address this limitation as the increased surface-to-volume ratio can facilitate the contact of active materials with electrolyte for charge storage [2,5–7].

Tungsten oxide nanostructures can be fabricated by various methods, including thermal evaporation, electron-beam/pulsed-laser/arc-discharge/chemical vapor deposition and solvothermal/sol-gel/electrochemical synthesis [8]. Among these processes, electrochemical fabrication is a very attractive method thanks to the variety of

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electrochemical techniques and their easily controlled parameters, which enables diverse nanostructure construction. For example, a nanoporous WO<sub>3</sub> thin film was deposited through a modified pulse electrochemical deposition, in which process an interval with defined time was set between each pulse. The WO<sub>3</sub> displayed excellent electrochromic performance due to the nanoscale interconnecting network of flaky WO<sub>3</sub> particles in the deposited film [9]. A “nano to nano” electrodeposition approach was designed for high performance electrochromic material via a process of cathodic reduction of WO<sub>3</sub> nanoparticles. This provided a good way to fabricate nano-structured thin films from the dispersion of nano-objects [10]. Mai and coworkers recently demonstrated the electrodeposition of nanoflower-like WO<sub>3</sub>, which displayed a quite high areal specific capacitance of 684 mF cm<sup>-2</sup> at 6 mA cm<sup>-2</sup> for pure tungsten oxide. It can retain 71.6% of its capacitance when the discharge current increased 2.3 times [2].

Tungsten oxides are also excellent electrochromic materials, endowing them potential electrode materials for smart supercapacitors through combining pseudocapacitive and electrochromic effects [11–13]. However, although tungsten oxides are very attractive functional materials, developments of high performance nanostructured tungsten oxides are very limited [1–5]. In this work, we designed a potential-limited pulse galvanostatic method (PLPG) to fabricate interconnected tungsten bronze nanosheets on partial exfoliated graphite (Ex-GF) substrate. There are plenty voids among the nanosheets. Thus fluent electrolyte penetration channels can be established to address the low capacitance contribution problems of the bulk materials. Benefiting from the merits of this novel architecture and the high electronic conductivity of tungsten bronze, the afforded WO<sub>3</sub>/Ex-GF exhibited excellent pseudocapacitive properties with a high specific capacitance of 5.95 F cm<sup>-2</sup> (495.8 F g<sup>-1</sup>) at 2 mA cm<sup>-2</sup> and a good rate capability, its capacitance at the high current density of 100 mA cm<sup>-2</sup> is as large as 3.57 F cm<sup>-2</sup> (297.5 F g<sup>-1</sup>). The asymmetric supercapacitor (ASC) assembled by using WO<sub>3</sub>/Ex-GF as negative electrode was able to deliver a high volumetric energy density of 2.88 mWh cm<sup>-3</sup> at the power density of 11.1 mW cm<sup>-3</sup>. The device also demonstrated a good cycling stability with 96.6% capacitance retained after 5000 galvanostatic charge/discharge cycles.

## 2. Experimental

### 2.1. Reagents and materials

All the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Graphite foils (GF) are obtained from SGL group (German).

### 2.2. Electrochemical deposition of tungsten bronze and MnO<sub>2</sub>

Before electrochemical depositions of tungsten bronze and MnO<sub>2</sub>, partial exfoliation of graphite foil (GF) was conducted on a multi-channel electrochemical analyzer (VMP3, Bio-Logic-Science Instruments, France), to afford partial exfoliated graphite foil (Ex-GF), by two steps as described in our previous report [14]. In the first step, the GF was potential dynamically scanned between 0.5 and 1.8 V at 20 mV s<sup>-1</sup> rate in 0.5 M K<sub>2</sub>CO<sub>3</sub> for 6 cycles, with a platinum plate and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. Then advanced cyclic voltammetry was conducted from -0.9 to 1.9 V at 20 mV s<sup>-1</sup> in 1 M KNO<sub>3</sub> for 10 cycles, during which the potential was held at 1.9 V for 5 s at the end of each cycle.

To prepare the electrolyte solution for the electrochemical deposition of tungsten bronze on Ex-GF, 0.0824 g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was dissolved in 20 ml deionized water, then 0.54 ml sulphuric acid and 0.05 ml H<sub>2</sub>O<sub>2</sub> was added under magnetic stirring. Tungsten bronze was deposited by a potential-limited pulse galvanostatic method (PLPG) with a SCE and a piece of GF as reference and counter electrodes, respectively. The pulse current was switched between -100 and

100 mA cm<sup>-2</sup>. The duty length was controlled by potential instead by time. For one deposition cycle, a square waveform pulse at -100 mA cm<sup>-2</sup> was first applied on the working electrode with the potential limit of -0.6 V. Then another square waveform pulse was followed at 100 mA cm<sup>-2</sup> with the potential limit of 0.6 V. A whole deposition procedure involved 2600 such cycles to afford WO<sub>x</sub>/Ex-GF. MnO<sub>2</sub>/Ex-GF was similarly prepared by PLPG with the pulse current of ± 100 mA cm<sup>-2</sup> in a solution containing 0.1 M Mn(Ac)<sub>2</sub> and 0.1 M NaSO<sub>4</sub>. The PLPG was conducted for 2800 cycles with the potential limit of ± 1.4 V.

### 2.3. Assembly of WO<sub>x</sub>/Ex-GF//MnO<sub>2</sub>/Ex-GF supercapacitor

A model asymmetric supercapacitor (ASC) of WO<sub>x</sub>/Ex-GF//MnO<sub>2</sub>/Ex-GF was assembled by using the gel electrolytes of H<sub>2</sub>SO<sub>4</sub>/polyvinyl alcohol (PVA) and LiCl/PVA in negative and positive electrodes, respectively with a piece of filter paper soaked by KCl/PVA gel as separator. The gel electrolytes were prepared according to literature reports [5,15]. Before ASC assembling, the as-prepared WO<sub>x</sub>/Ex-GF and MnO<sub>2</sub>/Ex-GF electrodes were immersed into 0.5 M H<sub>2</sub>SO<sub>4</sub> and 5 M LiCl electrolyte for 3 h, respectively. Then WO<sub>x</sub>/Ex-GF, MnO<sub>2</sub>/Ex-GF and a piece of filter paper were soaked in H<sub>2</sub>SO<sub>4</sub>/PVA, LiCl/PVA and KCl/PVA for 5 min and solidified at room temperature for 6 h, respectively. Then they were assembled together with the filter paper in between the WO<sub>x</sub>/Ex-GF and MnO<sub>2</sub>/Ex-GF. The entire device was wrapped with polyimide tape.

### 2.4. Characterization

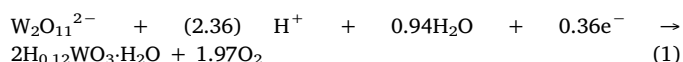
Morphologies and structures of the samples were investigated by scanning electron microscopy (SEM, hitachi su8010, Tokyo, Japan) and X-ray diffraction (XRD, Siemens D500/D501 with Cu K<sub>α</sub> radiation). Pseudocapacitive properties of the WO<sub>x</sub>/Ex-GF and MnO<sub>2</sub>/Ex-GF were studied by cyclic voltammetry and galvanostatic charge-discharge in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 5 M LiCl aqueous electrolytes, respectively in a conventional three-electrode configuration with SCE as the reference electrode. Electrochemical measurements of the model ASC were conducted in a two electrode configuration.

## 3. Results and discussions

### 3.1. Potential-limited pulse galvanostatic deposition of tungsten bronze

A potential-limited pulse galvanostatic method (PLPG) was designed in this work to deposit tungsten bronze on partially exfoliated graphite foil (Ex-GF) substrate. The XRD patterns of the product were shown in Fig. 1a. Characteristic diffractions corresponding to H<sub>0.12</sub>WO<sub>3</sub>·H<sub>2</sub>O (JCPDS 40-0693) can be seen in Fig. 1a, including those at 2θ = 12.82, 23.90, 27.23, 35.45 and 56.09°, showing that hydrogen tungsten bronze was obtained.

Dimeric peroxytungstate [(O<sub>2</sub>)<sub>2</sub>W(O)·O·W(O)(O<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> (W<sub>2</sub>O<sub>11</sub><sup>2-</sup>) was formed when preparing the electrolyte solution for tungsten bronze deposition by dissolving Na<sub>2</sub>WO<sub>4</sub> in the acidic H<sub>2</sub>O<sub>2</sub> solution, in which the tungsten is in +VI oxidation state [9]. During the electrochemical deposition, the tungsten was reduced in the cathodic pulse to afford hydrogen tungsten bronze in acidic solution according to the following reaction:



In the PLPG deposition, the duty length was controlled by potential limit. So the duty time may be different for different cycles. The anodic duty time in different cycles are shown in Fig. 1b. As can be seen, the anodic duty time increased slowly along with the deposition in the first ca. 1500 cycles. In the subsequent cycles, it increased sharply to ca.

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