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Highly efficient electro-optically tunable smart-supercapacitors using an oxygen-excess nanograin tungsten oxide thin film

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ABSTRACT

A smart supercapacitor shares the same electrochemical processes as a conventional energy storage device while also having electrochromic functionality. The smart supercapacitor device can sense the energy storage level, which it displays in a visually discernible manner, providing increased convenience in everyday applications. Here, we report an electro-optically tunable smart supercapacitor based on an oxygen-rich nanograin WO_3 electrode. The nanostructured WO_3 electrode is dark blue in color in the charged state and becomes transparent in its discharged state with a high optical modulation of 82%. The supercapacitor has a specific capacitance of 228 F g^{-1} at 0.25 Ag^{-1} with a large potential window (1.4 V). It is highly durable, exhibits good electrochemical stability over 2000 cycles, retains 75% of its initial capacitance, and exhibits high coloration efficiency (~170 cm^2/C). The excellent electrochromic and electrochemical supercapacitor properties of the electrode is due to the synergetic effect between nanograin morphology and excess oxygen. A smart-supercapacitor fabricated with an oxygen-rich nanograin WO_3 electrode exhibits a superb combination of energy storage and highly-efficient electrochromic features in one device that can monitor the energy storage level through visible changes in color.

1. Introduction

As the demand for advanced electronic devices increases, it is inevitable that greater functionality is integrated into energy storage devices in order to support the growing range of applications in portable electronics. While using an electronic device, it would certainly be useful and advantageous if the user could determine the amount of energy that has been consumed before the device stops working. Various transition metal oxides, such as WO_3 [1–14], TiO_2 [15–17], Nb_2O_5 [18–20], V_2O_5 [21,22] and NiO [23–33] show electrochromic behaviors that are determined largely by ion intercalation and deintercalation processes. This electrochemical mechanism is similar to the operating principle of an electrochemical supercapacitor. Thus, electrochromic (or smart) supercapacitors fill the niche of advanced electronic devices by functioning as a normal supercapacitor to store energy, and also by sensing the energy storage level through a change in the visual color (visualization of the device charge state as the degree of color saturation) [34–39]. In general, in order to maximally enhance electrochromic and supercapacitive performances, more complex electrode materials need to be used. However, for complex compound electrodes with high performance such as $W_{18}O_{49}$/PANI composite [35], $WO_3/ZnWO_4$ compounds [4], and PANI/WO_3 nanocomposite [41], reproducibility and reliability in fabrication and performance are challenging issues. Thus, it is desirable to obtain smart supercapacitor electrode materials that are reliable, earth-abundant, and easy to fabricate with a conventional technique.

Pure WO_3 is a well-known electrochromic material showing fast redox reaction, good chemical stability, and strong adherence to the substrate [33,35,40,41]. However, its potential application for a smart supercapacitor has not yet been fully explored. This is presumably because its electrochemical energy storage properties are anticipated to be unsatisfactory. The nanostructured morphologies of electrode materials can be very beneficial to enhance electrochemical reactions and efficiency. Herein, we employ a nanograin WO_3 film as a bifunc-

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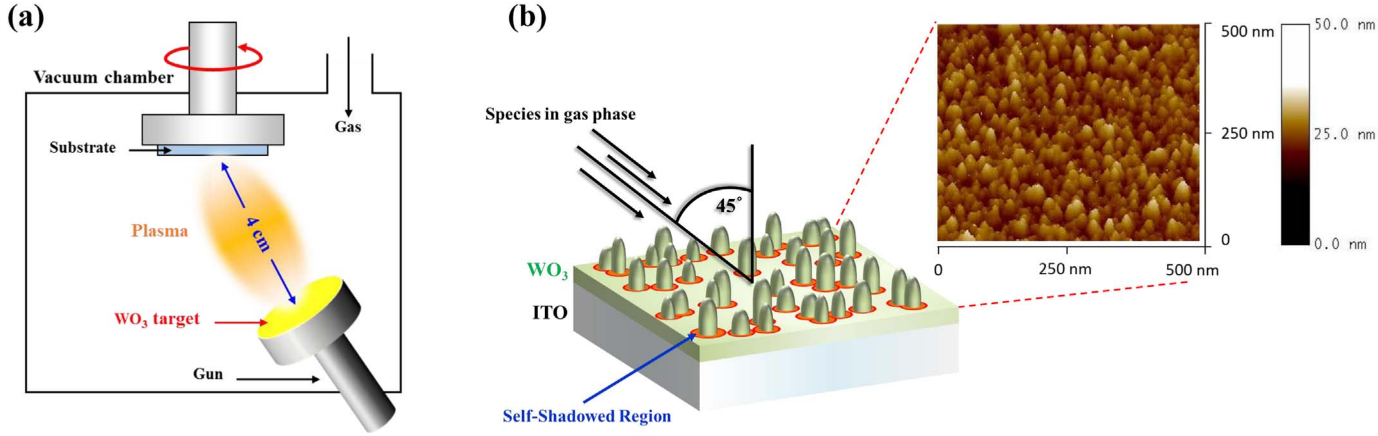

Fig. 1. Nanogranular growth of tungsten oxide during sputtering. (a) Schematic illustrations of RF-magnetron sputtering in which the angle and distance between target and substrate is 45° and 4 cm respectively. (b) 3-dimensional view showing growth of nanograin WO_3 electrode film together with an actual AFM image of a sample.

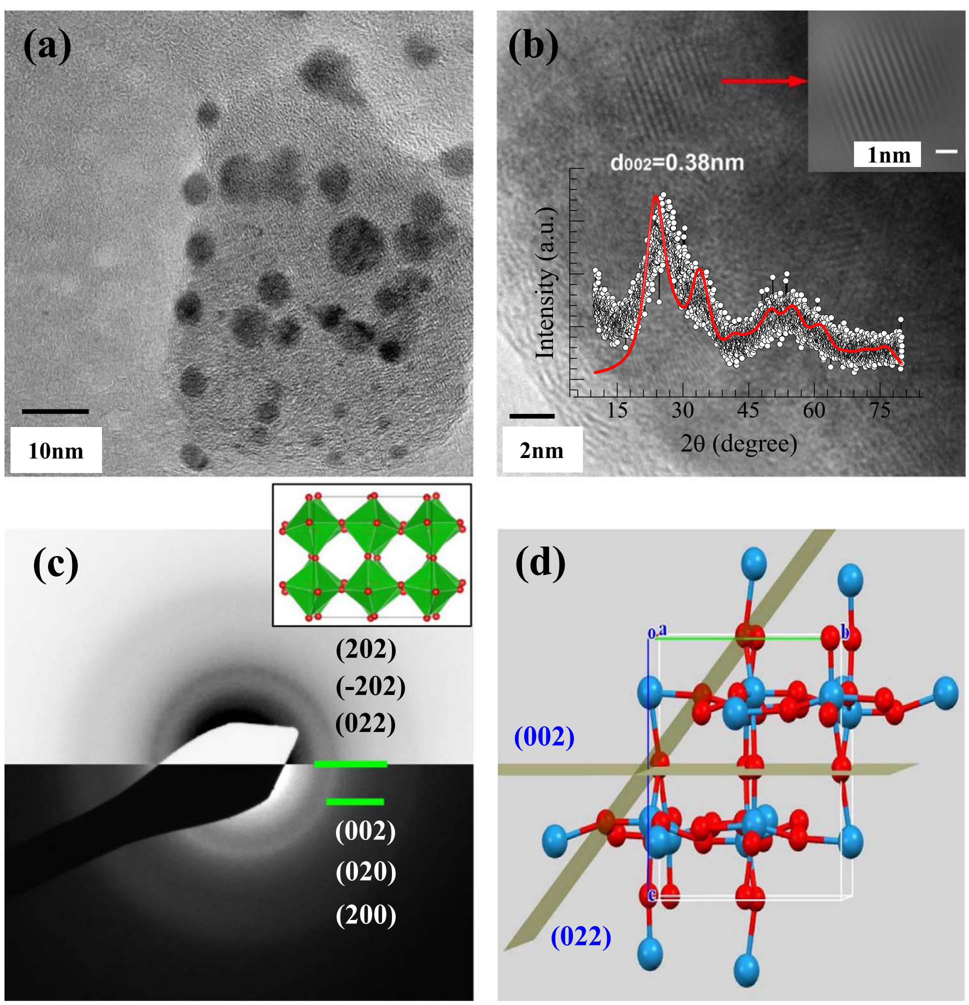

Fig. 2. (a) TEM and (b) HR-TEM images with 10 and 2 nm scale bars, respectively. The inset shows the X-ray nature of the synthesized film. The SAED pattern of the corresponding film is shown in (c), and the inset shows that the monoclinic WO_3 phase is mostly comprised of corner-linked octahedra of 4-membered channels along all crystallographic directions. The 002 and 022 crystallographic planes obtained from the SAED patterns are projected in (d). All crystallographic projections are made with the VESTA structure drawing software.

tional electrode for smart supercapacitor devices. The nanograin WO_3 layer was fabricated via oblique-angle sputtering and exhibited excellent electrochromic and supercapacitive properties owing to the large specific surface area as well as the monoclinic phase which facilitates electrochemical ion-insertion/extraction reactions and efficiency. Using a nanograin WO_3 electrode in a half cell configuration, excellent coloration efficiency (~170 $cm^2\ C^{-1}$) and good specific capacitance (228 F g^{-1} at 0.25 A g^{-1}) are achieved.

2. Experimental section

Oxygen-excess nanograin WO_3 thin film electrodes were fabricated on ITO-coated conducting glass substrates with a sheet resistance of 27 Ω cm^{-2} using conventional radio frequency (RF) magnetron sput-