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Citation for final published version:

Kim, Jongmin, Inamdar, Akbar I., Jo, Yongcheol, Cho, Sangeun, Aqueel Ahmed, Abu Talha, Hou, Bo , Cha, SeungNam, Kim, Tae Geun, Kim, Hyungsang and Im, Hyunsik 2020. Nanofilament array embedded tungsten oxide for highly efficient electrochromic supercapacitor electrodes. Journal of Materials Chemistry A 8 (27) , pp. 13459-13469. 10.1039/D0TA01728K

Publishers page: http://dx.doi.org/10.1039/D0TA01728K

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## Nanofilament array embedded tungsten oxide for highly

## efficient electrochromic supercapacitor electrodes

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**ABSTRACT**: The high-activity of metallic nanofilament array (NFA) embedded tungsten oxide (WO<sub>3</sub>) bifunctional electrodes for electrochromism and electrochemical energy storage is presented. The NFA reduces charge transfer resistance and increases the electrochemically active surface area at the electrode–electrolyte interface. The NFAembedded WO<sub>3</sub> electrode exhibits a specific capacity of 214 F g<sup>-1</sup> (pristine WO<sub>3</sub>: 133 F g<sup>-1</sup>) at 0.25 mA cm<sup>-2</sup>, excellent cycling stability with ~92% capacitance retention after 2000 cycles (pristine WO<sub>3</sub>: ~75% capacitance retention) and a coloration efficiency of 128 cm<sup>2</sup> C<sup>-1</sup> (pristine WO<sub>3</sub>: 91 cm<sup>2</sup> C<sup>-1</sup>) with superb optical modulation. These properties are significantly more advanced compared to the pristine WO<sub>3</sub> electrode and superior to previously reported WO<sub>3</sub>based composites and nanostructured materials.

KEYWORDS: Nanofilament array; tungsten oxide; electrochromism; supercapacitor.

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Since the concept of "nanoscience" was first introduced in the 1960s, nanomaterials and nanotechnologies have been rapidly applied in numerous industries and fundamental research fields. In particular, as both energy demand and consumption have increased tremendously in diverse fields ranging from heavy industry to transportation to portable electronic devices, nanoscience has been exploited not only to enhance the performance of various energy storage and harvesting devices but also to use energy sources efficiently.<sup>1,2</sup> Considerable efforts have been devoted to advancing renewable and clean technologies combined with many natural energy sources for energy storage and mobile power generation. Smart supercapacitors, also called electrochromic supercapacitors, represent an attractive technology that provides superior power density with additional electrochromic functionalities.<sup>3-5</sup> The electrode material is a key element of a smart supercapacitor and is the primary determiner of its ultimate performance.

Smart supercapacitors exploit electrochemical and electrochromic processes at the electrode–electrolyte interface and because these processes share a similar redox chemical reaction mechanism at the interface, the energy storage levels can be observed by monitoring the color of the active electrode. In general, a high-performance smart supercapacitor electrode exhibits the following attributes: a large electrochemically active surface area, high electrical conductivity, high ionic transport rate, and high electrochemical durability. The common technology strategy for developing high-performance electrodes is to fabricate hybrid composite materials whose constituting materials produce synergetic effects that enhance the four aforementioned attributes for improved performance.

Because of a high degree of color tailorability, state-of-the-art smart supercapacitors are fabricated using oxide/hydroxide-based materials which typically exhibit a high power density, fast charge/discharge rate, good safety, and long cycle life.<sup>6-9</sup> Among electrochromic oxide materials, tungsten oxide (WO<sub>x</sub>,  $x \approx 3$ ) has attracted widespread attention because of its fast color switching and high coloration efficiency.<sup>10-12</sup> In addition, WO<sub>x</sub> composite films containing

additives, for example, Nb dopant ions,<sup>13</sup> lithium phosphorous oxynitride,<sup>14</sup> or reduced graphene oxide<sup>15</sup> have been investigated to improve electrochromic properties. On the contrary, pure bulk WO<sub>x</sub> shows poor electrochemical performance and stability as a supercapacitor electrode. Numerous attempts to enhance its electrochemical activities through the development of hybrid composite materials such as WO<sub>3</sub>/carbon aerogels,<sup>16</sup> polyaniline/WO<sub>3</sub>,<sup>17</sup> WO<sub>3-x</sub>/MoO<sub>3-x</sub>,<sup>18</sup> WO<sub>3</sub>/Ag/WO<sub>3</sub>,<sup>19</sup> and WO<sub>3</sub>/TiO<sub>2</sub>,<sup>20</sup> have been reported.

In the present work, we present a unique but generally applicable method to enhance both the electrochemical and electrochromic properties of a metal oxide-based smart supercapacitor electrode by embedding a nanoscale metallic nanofilament array (NFA), formed via an electroforming process, across a dielectric insulator electrode.<sup>21-23</sup> The NFA improves the electrochemical activity at the surface and the bulk electrical conductivity, substantially enhancing both the electrochromic and the electrochemical energy storage properties of the metal oxide.

Amorphous tungsten oxide (WO<sub>3</sub>) thin-film electrodes were deposited onto indium tin oxide (ITO)-coated conducting glass substrates using a conventional radio frequency (RF) magnetron sputtering system with a pure tungsten oxide target. The thicknesses of the tungsten oxide films were measured using field-emission scanning electron microscopy (FE-SEM) and estimated to be ~250 nm (Fig. S1c). The actual chemical compositions of the WO<sub>3+ $\Box$ </sub> films were determined by Rutherford backscattering spectroscopy (RBS) measurements, as shown in Fig. S1d. The  $\Box$  value was measured to be 0.191, indicating the presence of excess oxygen, which is associated with negative ion effects during sputtering.<sup>24</sup>

Fig. 1a is a schematic of a metallic NFA embedded in a WO<sub>3</sub> film. The array was fabricated by electroforming WO<sub>3</sub> using a parameter analyzer (Keithley 4200-SCS) with a twoprobe system, where Au tips contacted the WO<sub>3</sub> film and the conducting ITO substrate. Moreover, the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> films have a similar surface morphology (Fig. S1a and b). When a positive voltage was applied, the leakage current also increased; however, beyond a critical voltage, the current abruptly increased (Fig. S4a). This phenomenon is known as "electroforming". After the electroforming process, the insulating WO<sub>3</sub> film showed reversible bi-stable resistance states between the high-resistance state (HRS) and the low-resistance state (LRS). Fig. 1b shows the measured resistive switching characteristics. This observed resistive switching behavior is typical of unipolar resistive switching.<sup>25</sup> The resistive switching points are spaced 500  $\mu$ m apart while within the electrode area of 1 cm  $\times$  1 cm, 300 resistive switching points are formed. Fig. 1c shows the distribution of the measured resistance. The resistive switching mechanism is explained by the reversible creation and rupture of nanofilamentary paths via a redox chemical reaction (see Fig. S3 for more details).<sup>26</sup> The resistance retention characteristics of the LRS is evaluated at a constant readout voltage of 0.1 V. Fig. S4b shows the time-dependent current fluctuation in the LRS for the WO<sub>3</sub> electrode with an NFA at room temperature. The LRS retention is found to be very stable for over 30,000 s, demonstrating a non-volatile low-resistance behavior for enhanced charge transfer dynamics at the electrode–electrolyte interface.<sup>27</sup>

Fig. 1d and e show the X-ray photoelectron spectroscopy (XPS) spectra of the pristine (before electroforming) and NFA-embedded WO<sub>3</sub> electrodes surfaces, respectively. For the pristine WO<sub>3</sub> electrode, three binding-state peaks are observed at 33.5 eV, 34.2 eV, and 36.3 eV, which correspond to the W<sup>5+</sup> and W<sup>6+</sup> oxidation states. By contrast, the WO<sub>3</sub> with an NFA shows four binding-state peaks at approximately 30.1 eV (W<sup>0</sup>), 32.2 eV (W<sup>4+</sup>), 33.5 eV (W<sup>5+</sup>), and 36.3 eV (W<sup>6+</sup>).<sup>28,29</sup> Carbon (C) 1s photoelectrons with a binding energy of 285.0 eV were used for reference purposes.<sup>30</sup> After electroforming, the magnitude of the two major insulating binding states of W<sup>6+</sup> and W<sup>5+</sup> decreased; however, the metallic (or semiconducting and metallic) binding-state peaks of W<sup>4+</sup> and W<sup>0</sup>, which were not detected in the spectrum of the pristine WO<sub>3</sub> electrode, clearly appeared in the spectrum (Table S1). The existence of the

metallic binding state of W<sup>0</sup> suggests that metallic conducting channels are formed across the film, improving the electrical conductivity of the pristine WO<sub>3</sub> electrode.<sup>31,32</sup> Fig. S2 shows the O1s peak of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> films. The main peak can be deconvoluted into two peaks at 529.3 eV and 530.2 eV that correspond to the lattice oxygen and non-lattice oxygen, respectively. The amount of oxygen vacancies is proportional to the ratio of non-lattice oxygen. For the NFA-embedded WO<sub>3</sub> electrode, the percentage of non-lattice oxygen increases, indicating high-density oxygen vacancies in the film. The depth-profile XPS spectra taken from various resistive switching metal oxides that exhibit similar unipolar resistive switching behaviors confirm that metallic binding states are formed vertically across the bulk metal oxide film rather than only on the surface.<sup>33</sup> On the contrary, substantial changes in the binding states of W were not detected after LRS  $\leftrightarrow$  HRS switching, implying that the LRS  $\leftrightarrow$  HRS switching is determined by the microscopic chemical redox reaction in W–O binding states in the nanoscale region.<sup>34,35</sup>

Using transmission electron microscopy (TEM), we confirmed the existence of nanofilaments embedded in the WO<sub>3</sub>. The presence of Moiré fringes explains the structural changes of the WO<sub>3</sub>, indicating the formation of conducting nanofilamentary paths (Fig. 1f).<sup>36</sup> These superposed paralleled lattice planes, which induce Moiré fringes, originate from the rearrangement of oxygen vacancies during the electroforming process which result in different lattice spacing. Indeed, the high-resolution TEM (HR-TEM) image clearly shows interplanar spacings of 0.36 nm and 0.22 nm, which correspond to WO<sub>3</sub> and metallic W respectively (Fig. 1g). The observed microscopic structural changes in WO<sub>3</sub> are associated with the migration of oxygen ions under a high-voltage bias.<sup>37</sup> After the electroforming process, the selected-area

electron diffraction (SAED) pattern showed diffraction rings, demonstrating the polycrystalline nature of the prepared materials.<sup>38,39</sup> Furthermore, we resolve not only the (200), (202), (222), and (400) planes of the WO<sub>3</sub> phase but also the (110) plane of metallic W (Fig. S1e). Fig. 1h shows the conductive-AFM image used to investigate the local conductivity distribution of the WO<sub>3</sub> electrode. Conductive paths were observed after the electroforming process, indicating the formation of nanofilaments across the WO<sub>3</sub> film.<sup>40</sup>

The supercapacitor properties of the electrode materials were studied using cyclic voltammetry (CV). The CV curves of pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> were recorded at different scan rates ranging from 5 to 100 mV s<sup>-1</sup> in a 1 M LiClO<sub>4</sub> + PC electrolyte between -0.9 and 0.5 V (vs. SCE), as shown in Fig. 2a and c. With increasing scan rate, the quasi-rectangular CV shape becomes deformed; this phenomenon is associated with the slow charge–discharge kinetics and diffusion limitation at the electrode–electrolyte interface.<sup>41</sup>

Fig. 2b and d show the stability tests for 2000 cycles at a scan rate of 100 mV s<sup>-1</sup>. For the NFA-embedded WO<sub>3</sub> electrode, the observed area under the curve is larger and more stable than that obtained from the pristine WO<sub>3</sub> electrode; this difference is partly associated with the greatly improved bulk electrical conductivity caused by the metallic nanofilaments across the WO<sub>3</sub> film. The specific capacitance ( $C_s$ ) of the WO<sub>3</sub> electrodes can be calculated from the area under the CV curve using the following equation:<sup>42,43</sup>

$$C_s = \frac{1}{2\nu m\Delta V} \int I dV \ (1)$$

where v is the scan rate (mV s<sup>-1</sup>), m is the mass of the electrode film (g),  $\Delta V$  is the potential window, and IdV is the area under the CV curve. Fig. 2e shows the specific capacitance of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes as a function of scan rate v. For both electrodes, the calculated specific capacitance increases gradually with decreasing scan rate, which is attributed to the facile diffusion of the electrolytic ions at low scan rates.<sup>44,45</sup>Furthermore, the NFA-embedded WO<sub>3</sub> electrode shows a substantially improved specific capacitance compared to the pristine WO<sub>3</sub> electrode at the same scan rate. In particular, the maximum specific capacitance of the pristine  $WO_3$  and NFA-embedded WO<sub>3</sub> electrodes is 139 and 202 F g<sup>-1</sup> at 5 mV s<sup>-1</sup>, respectively. Most surprisingly, the NFA-embedded WO<sub>3</sub> electrode exhibits superior long-term cycling performance. Fig. 2f shows the measured cycling stability of the pristine WO<sub>3</sub> and NFAembedded WO<sub>3</sub> electrodes for up to 2000 cycles at a scan rate of 100 mV s<sup>-1</sup>. The pristine WO3 electrode shows ~75% capacitance retention after 2000 cycles, whereas the NFAembedded WO3 electrode exhibits excellent long-term cycling stability with ~92% retention of its initial specific capacitance. In addition, the cycle performance for the pristine WO3 and NFA-embedded WO3 electrodes was measured up to 10000 cycles at an increased scan rate of 150 mV s<sup>-1</sup> (Fig. S4c). It was found that the NFA- embedded WO<sub>3</sub> electrode is more stable (~96%) than the pristine WO3 electrode (~89%). These results suggest that the NFA-embedded WO<sub>3</sub> electrode can significantly enhance cycling performance because the conducting nanofilamentary paths serve as conductive networks that enable efficient electron transport during long-term cycling.

The CV data also provide the kinetics of the electrode reaction at various sweep rates according to the following equation:<sup>46</sup>

$$(2)$$

$$i = av^b$$

where *a* is a constant, *i* is the measured anodic peak current, and *v* is the scan rate. The value of parameter *b* can be determined from the slope of the log(v)-log(i) plot. A *b* value of 0.5 indicates that the redox process is controlled by a diffusion process, whereas a value of 1.0 indicates a surface-capacitive controlled process.<sup>47</sup> As shown in Fig. S4d, the calculated *b* value of the peakanodic current is between 0.5 and 1, indicating that both a surface capacitive effect and Li<sup>+</sup> intercalation reaction contribute to the measured current.

To further quantitatively analyze the pseudocapacitive contribution, we further model the reaction kinetics using the following equation:<sup>48</sup>

$$i(V) = k_1 V + k_2 V^{\frac{1}{2}}$$
(3)

where i(V) is the current response at a fixed potential, v is the scan rate, and  $k_1$  and  $k_2$  are

adjustable values. Fig. 3a shows plots of  $i/v^{1/2}$  versus  $v^{1/2}$  for the pristine WO<sub>3</sub> and NFAembedded WO<sub>3</sub> electrodes at 0.1 V. By calculating both  $k_1$  and  $k_2$ , we could distinguish the contribution ratio of the capacitive effects ( $k_1v$ ) and the diffusion-controlled insertions ( $k_2v^{1/2}$ ) at specific potentials. Fig. 3b shows the calculated contribution ratio at various scan rates for the electrodes. These results reveal that the percentage of capacitive contributions increases with increasing scan rate. For the pristine WO<sub>3</sub> electrode, as the scan rate increases the redox reaction at the surface is also enhanced, increasing the capacitive effect. In addition, the capacitive contribution of the NFA-embedded WO<sub>3</sub> electrode is greater than that of the pristine WO<sub>3</sub> electrode at all scan rates. This is because electroforming-induced negatively charged oxygen ions on the electrode surface can enhance the absorption of Li<sup>+</sup> at the electrode/electrode interface. Fig. 3c–f show the capacitive contributions (the shaded region) at both 5 and 80 mV s<sup>-1</sup>. The larger capacitive contribution value of the NFA-embedded WO<sub>3</sub> electrode suggests that it participates in a fast redox reaction during the electrochemical process.<sup>49</sup> The fast redox reaction of the NFA-embedded WO<sub>3</sub> electrode is associated with fast electron transfer kinetics, which provides excellent pseudocapacitive properties.

The accessible electrochemical reaction surface area can be estimated by analyzing the electrochemically active surface area (ECSA). Fig. 4a and b show the CV curves of the pristine  $WO_3$  and the NFA-embedded  $WO_3$  electrodes in the non-faradaic region. The scan rate (*v*)-dependent capacitive current ( $I_{DL}$ ) is obtained from the non-faradaic region as follows:<sup>50</sup>

$$I_{\rm DL} = C_{\rm DL} \times v$$

where  $C_{DL}$  is the double-layer region-specific capacitance that corresponds to the slope of the  $I_{DL}$  characteristics. Fig. 4c shows the  $I_{DL}$  at 0.3 V. The ECSA of the electrode was calculated according to the equation:<sup>51</sup>

$$ECSA = C_{\rm DL}/C_{\rm S}$$

where  $C_s$  (0.035 mF cm<sup>-2</sup> for H<sub>2</sub>SO<sub>4</sub>) is the specific capacitance of the electrolyte. The

calculated ECSA value for the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes is 10.1 and 71.7 cm<sup>2</sup>, respectively. The observed higher ECSA value for the NFA-embedded WO<sub>3</sub> electrode suggests that electroforming-induced low-oxygen (WO<sub>x</sub>, 0 < x < 3) surface chemical states are naturally favorable to electrochemical reactions and activity.<sup>52</sup>

We investigated the charge–discharge dynamics of the electrodes by measuring their galvanostatic charge–discharge (GCD) characteristics at various current densities (0.25–1 mA cm<sup>-2</sup>). The potential window was fixed from –0.9 to 0.45 V (vs. SCE). Fig. 5a and b show the recorded charge–discharge curves, which exhibit typical pseudocapacitive behaviors, confirming that faradaic reactions are responsible for the charge storage.<sup>53</sup> The specific capacitance of the electrodes can be calculated using their galvanostatic discharge curves by the following equation:<sup>54</sup>

where *I* is the response current and  $\Delta t$  represents the discharge time. Fig. 5c presents the calculated specific capacitance of the electrodes at different current densities. The decrease of specific capacitance with increasing current density is due to the poor penetration and diffusion

of the electrolyte.<sup>55</sup> The maximum specific capacitance for the pristine WO<sub>3</sub> and NFAembedded WO<sub>3</sub> electrodes is 133 and 214 F g<sup>-1</sup> at 0.25 mA cm<sup>-2</sup>, respectively. The obtained specific capacitance of the NFA-embedded WO<sub>3</sub> electrode is much higher than that of the pristine WO<sub>3</sub> electrode by ~ 61%. The coulombic efficiencies ( $\eta$ ) of all the electrodes exhibit ~99% at various current densities. There is a slight variation in the specific capacitance from the CV and GCD curves. This is because the specific capacitance obtained by CV is calculated at a particular potential, while that obtained from the GCD is an average capacitance over the potential range.<sup>56</sup>

From the galvanostatic charge–discharge curves, the gravimetric energy density (*E*) and power density (*P*) can be calculated from the following formulas:<sup>57,58</sup>

$$E = \frac{1}{2}C_s\Delta V^2 \quad (7)$$
$$P = \frac{E}{\Delta t} (8)$$

where  $\Delta V$  is the voltage range and  $\Delta t$  is the discharge time. Fig. 5d presents the calculated power density as a function of energy density (Ragone plot) and it can be seen that the NFA-embedded WO<sub>3</sub> electrode shows higher energy and power densities compared to the pristine WO<sub>3</sub> electrode. To further evaluate the electrochemical energy storage performance of the electrodes, asymmetric supercapacitors were assembled using the WO<sub>3</sub> electrode as a positive electrode and carbon (C) as a negative electrode (Fig. S5a). The asymmetric supercapacitor devices were tested in a two-electrode cell with a 1 M LiClO4 + PC

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electrolyte. The total amount of charge (Q) stored in each positive and negative electrode

must be equal and it is given by the following equations:

$$Q_+ = Q_-$$

(10)

$$(m_+) \times (i_+) \times \Delta t_+ = (m_-) \times (i_-) \times \Delta t$$

where *m* represents the loading mass, *i* indicates the delivered current, and  $\Delta t$  is the discharge time of the individual electrodes. The + and – signs are used in the subscript to denote the positive and negative electrodes, respectively. The charge/discharge curves were recorded in a wide potential window range between -0.9 and 0.45 V. Fig. S5b and c show the charge–discharge profiles of the pristine WO3//C and NFA- embedded WO3//C asymmetric devices. Clearly, the NFA-embedded WO3//C device shows a longer discharge time compared to the pristine WO3//C asymmetric device. The obtained results were plotted in the Ragone plot, as shown in Fig. S6. The NFA- embedded WO3//C asymmetric supercapacitor shows higher energy and power densities than the pristine WO3//C device.

We further investigated changes in the interfacial properties of the electrodes after longterm stability testing using EIS analysis in the frequency range from 10 kHz to 0.1 Hz. Fig. 5e and f show the Nyquist plots of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes before

(11)

and after 2000 CV cycles at a scan rate of 100 mV s<sup>-1</sup>. The equivalent circuit is shown as an inset in Fig. 5f. CPE represents the constant phase element. The intercept of the real impedance  $(Z_{re})$  in the high-frequency region of the Nyquist plot corresponds to the solution resistance  $(R_s)$ , which includes both the internal resistance of the electrode and the bulk resistance of the electrolyte.<sup>59</sup> The charge transfer resistance ( $R_{ct}$ ) can be obtained directly from the diameter of the semicircle in the high-frequency region.<sup>60,61</sup> The slope of a straight line in the low-frequency region corresponds to the Warburg impedance  $(Z_w)$  which is related to the diffusion of Li<sup>+</sup> ions into the electrode.<sup>62,63</sup> Fitted values for the main circuit parameters are listed in Table 1 and it can be seen that the  $R_s$  of the NFA-embedded WO<sub>3</sub> electrode is smaller than that of the pristine WO<sub>3</sub> electrode, which due to the enhanced conductivity associated with the conducting NFA. Furthermore, the EIS spectrum of the NFA-embedded WO<sub>3</sub> electrode exhibits almost no semicircle; its theoretically modelled  $R_{ct}$  value is 5.5  $\Omega$ , indicating very fast charge transfer between the electrode and the electrolyte. Before cycling, the NFA-embedded WO<sub>3</sub> electrode exhibited a large  $Z_w$  value because of the oxygen-ion migration in the electroforming process.<sup>64,65</sup> In particular, the  $R_s$ ,  $R_{ct}$ , and  $Z_w$  values of the pristine WO<sub>3</sub> electrode are much higher than those obtained for the NFA-embedded WO<sub>3</sub> electrode after 2000 cycles, explaining the observed low specific capacitance and poor stability of the pristine WO<sub>3</sub> electrode.<sup>66</sup>

The WO<sub>3</sub> material shows a favorable and reversible color change between transparent and blue. Compared with other electrochromic metal oxide materials, WO<sub>3</sub> exhibits a superior coloration efficiency (CE) and electrochromic response time.<sup>67</sup> The electrochromic process depends on the intercalation/deintercalation of Li<sup>+</sup> ions into/from the WO<sub>3</sub> electrode near the surface. The reaction mechanism can be represented as:<sup>68</sup>

$$WO_3 + xLi^+ + xe^-$$
 (discharged/transparent) $\leftrightarrow Li_xWO_3$  (charged/blue)

During the cathodic potential scan, the intercalation of Li<sup>+</sup> ions induces the reduction of the W<sup>6+</sup> state to the W<sup>5+</sup> state, resulting in the electrochromic effect (blue coloration of the film).<sup>[69,70]</sup> By contrast, during the anodic potential scan, an oxidation reaction at the electrode–electrolyte interface causes deintercalation of Li<sup>+</sup> ions from the W<sup>5+</sup> state to the W<sup>6+</sup> state, making the electrode transparent (bleached). To evaluate the electrochromic properties of both the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes, we conducted optical transmittance measurements by applying potential steps of ±0.75 V (vs. SCE) for a fixed time of 30 s. The transmittance spectra for the electrodes were recorded in the colored and bleached states, as shown in Fig. 6a and b. The optical density ( $\Delta OD$ ) was estimated at 630 nm using the following equation:

$$(\Delta OD) = \log\left(\frac{T_b}{T_c}\right) (12)$$

where  $T_{\rm b}$  and  $T_{\rm c}$  are the transmittance at the bleached and colored states, respectively. The optical modulation for the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes is found to be approximately 55% and 67%, respectively (Fig. S7a and b).

Fig. 6c and d show the chronocoulometry curves used to investigate the amount of intercalated ( $Q_i$ ) and deintercalated charge ( $Q_{di}$ ). The electrochromic reversibility ( $\Re$ ) was calculated according to the following equation:<sup>71</sup>

$$\Re(\%) = \frac{Q_{di}}{Q_i} \times 100$$

After electroforming, the electrochromic reversibility of the  $WO_3$  electrode increases considerably from 30 to 37%. The improved reversibility is associated with the electroforming

induced favorable surface states for the intercalation/deintercalation processes and is consistent with the enhanced electrochemical energy storage performance. The coloration efficiency is critical to electrochromic performance and can be calculated as:<sup>72</sup>

#### $CE = (\Delta OD)/Q/A$ (14)

where Q/A represents the amount of charge per unit area of the electrode's surface. The WO<sub>3</sub> electrode with NFA exhibits a remarkably improved CE of 128 cm<sup>2</sup> C<sup>-1</sup> compared to that obtained for the pristine WO<sub>3</sub> of 91 cm<sup>2</sup> C<sup>-1</sup> (Fig. S7c). The observed electrochromic performance is summarized in Table 2. As shown in Fig. 6e and f, the NFA-embedded WO<sub>3</sub> electrode, with superior CE, exhibits a darker blue color in the colored state at – 0.75 V.

In this work, we fabricated a tungsten oxide film electrode in which an electroforminginduced metallic NFA was embedded, and subsequently investigated its smart supercapacitor properties. The NFA-embedded WO<sub>3</sub> electrode demonstrated superior specific capacitance, long-term cycling stability, and CE compared to the pristine WO<sub>3</sub> electrode. This performance improvement is due to the synergetic effects between its enhanced bulk conductivity, increased electrochemically active surface area, and fast charge transfer kinetics. Our experimental findings could pave the way for a new powerful concept for smart supercapacitor applications and can further be extended to improve other electrodes for water electrolysis and batteries.

#### **Experimental section**

**Electrode fabrication:** We fabricated WO<sub>3</sub> electrode films using RF magnetron sputtering with a WO<sub>3</sub> target (99.99% purity). Before deposition, ITO-coated glass substrates were ultrasonically cleaned with acetone, methanol, and deionized water (10 min each) and then dried with N<sub>2</sub> gas. The chamber was initially evacuated to  $3.0 \times 10^{-6}$  Torr and maintained at 10 mTorr. During the process of deposition, an Ar/O<sub>2</sub> gas flow mixture ratio was maintained at 8:2 with a sputtering power of 120 W for 20 min. The area of the electrode film was  $1 \times 1$  cm<sup>2</sup> for electrochemical supercapacitor measurements and  $2 \times 2$  cm<sup>2</sup> for electrochromic measurements.

**Preparation of electrolyte:** The electrolyte was prepared by mixing lithium perchlorate (LiClO<sub>4</sub>) and propylene carbonate (PC) at room temperature. The LiClO<sub>4</sub> (5.315 g) was dissolved in 50 mL of PC using a magnetic stirrer for 10 min.

**Material characterization:** The thickness of a WO<sub>3</sub> electrode film was determined using fieldemission scanning electron microscopy (FE-SEM, Hitachi S-4800). To investigate the microscopic structural properties of WO<sub>3</sub> electrode films, high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-3000F) analysis was employed. The chemical binding states were studied using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI, Inc., Japan). The transmittance spectra were collected using visible and nearinfrared (VIS–NIR) spectroscopy (Tec5, Germany).

**Electrical characterization:** An NFA was formed across the  $WO_3$  electrode film via electroforming using a Keithley 4200-SCS semiconductor characterization system with two-probe electrical measurements. The diameter of the probe tip used in the experiments was 10  $\mu$ m.

**Evaluation of the electrochemical and electrochromic performances:** The electrochemical and electrochromic measurements were carried out using a potentiostat (Princeton Applied Research, VersaSTAT 3) with a standard three-electrode cell system in 1 M LiClO<sub>4</sub> + PC

electrolyte. The WO<sub>3</sub> electrodes were the working electrode. A saturated calomel electrode (SCE) and graphite were used as the reference electrode and counter electrode, respectively.

#### Acknowledgements

The authors would like to thank the financial support from the National Research Foundation (NRF) of Korea (Grant nos. 2016R1A3B1908249, 2016R1A6A1A03012877, 2018R1D1A1B07049046, 2018R1D1A1A09083859).

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**Fig. 1** (a) Schematic showing the formation of a conducting nanofilament array (NFA) across a WO<sub>3</sub> electrode film via an electroforming process. (b) Resistance-switching current–voltage (I-V) curves of the WO<sub>3</sub> film showing bi-stable resistance states. (c) The resistance distribution of the low- and high-resistance states extracted at a 0.1 V read voltage. XPS spectra of (d) the pristine WO<sub>3</sub> and (e) NFA-embedded WO<sub>3</sub> films. (f) Cross-sectional high-resolution TEM image of the NFA-embedded WO<sub>3</sub> film and (g) a magnified view showing the Moiré fringes. (h) Conductive-AFM image of the NFA-embedded WO<sub>3</sub> electrode measured with a compliance current of 10 nA.



**Fig. 2** (a, c) CV curves at various scan rates from 5 to 100 mV s<sup>-1</sup> and (b, d) after 2000 continuous cycles at a scan rate of 100 mV s<sup>-1</sup> for the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes. (e) Comparison of the specific capacitance measured at different scan rates. (f) Long-term cycling stability of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes at a scan rate of 100 mV s<sup>-1</sup>.



**Fig. 3** (a) Scan rate-normalized anodic current  $(i/v^{1/2})$  at 0.1 V as a function of  $v^{1/2}$ . The linear behavior between  $i/v^{1/2}$  and  $v^{1/2}$  indicates the pseudocapacitive nature of the active electrode material. (b) Relative contributions of the diffusive and capacitive currents to the CV curves at different scan rates. (c, e) CV response for the pristine WO<sub>3</sub> electrode at 5 mV s<sup>-1</sup> and 80 mV s<sup>-1</sup>, respectively. (d, f) CV response for the NFA-embedded WO<sub>3</sub> electrode at 5 mV s<sup>-1</sup> and 80 mV s<sup>-1</sup>, respectively. The shaded region represents the capacitive contribution to the total current.



**Fig. 4** (a, b) CV curves of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes at different scan rates in the nonfaradaic voltage region. (c) Nonfaradaic current density from the CV curves at 0.3 V as a function of the scan rate (mV s<sup>-1</sup>). The slope corresponds to the double-layer-region specific capacitance.



**Fig. 5** (a, b) GCD curves at different current densities for the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes, respectively. (c) Comparison of the specific capacitance measured at different current densities. (d) Ragone plot describing the relation between the measured specific power and the specific energy. Impedance spectra (Nyquist plots) of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes (e) before and (f) after 2000 cycles. The inset shows the equivalent circuit diagram.



**Fig. 6** (a, b) Transmittance spectra of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes at the colored and bleached states, respectively.  $\Delta T = T_b - T_c$  at a wavelength of 630 nm. (c, d) Chronocoulometry curves of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes, respectively. (e, f) Photos of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes at the colored (-0.75 V) and bleached (+0.75 V) states. The visual color indicates the level of energy stored in the electrode.

		Before cycling				After 2000 cycles			
	$R_{s}\left(\Omega ight)$	$R_{ct}\left(\Omega\right)$	CPE (µF)	$Z_{w}\left(\Omega\right)$		$R_{s}\left(\Omega\right)$	$R_{ct}\left(\Omega\right)$	CPE (µF)	$Z_{w}\left(\Omega\right)$
Pristine WO <sub>3</sub>	93	120.5	74	60.2		105.7	1970	37.0	2950
NFA- embedded WO <sub>3</sub>	80	5.5	100	230.7		91.9	247	361.5	386

**Table 1** Extracted circuit parameters obtained by modelling the recorded EIS curves.

**Table 2** Comparison of electrochromic performance parameters of the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes.

	Q <sub>i</sub> (mC/cm <sup>2</sup> )	Q <sub>di</sub> (mC/cm <sup>2</sup> )	Reversibility (%)	Transn (%	1smittance Optical Opti (%) modulation dens (%) (ΔΟ		Optical density	Coloration efficiency
				$T_{\rm b}$	$T_{\rm c}$	(70)	(20D)	(cm/c)
Pristine WO <sub>3</sub>	-36.17	10.84	29.96	97.13	42.47	54.65	0.82	91.46
NFA- embedded WO <sub>3</sub>	-39.10	14.58	37.28	94.51	27.01	67.49	1.25	128.10

#### Table of content

Nanofilament array embedded metal oxide for a highly efficient electrochemical

electrode



## **Supporting Information**

Nanofilament array embedded tungsten oxide for highly efficient electrochromic supercapacitor electrodes

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**Fig. S1** Top-view field-emission scanning electron microscopy (FE-SEM) images for (a) the pristine  $WO_3$  and (b) NFA-embedded  $WO_3$  films. (c) Cross-sectional FE-SEM image of the  $WO_3$  film. FE-SEM image showing the thickness of the  $WO_3$  film. (d) Rutherford backscattering spectroscopy (RBS) profiles of the  $WO_3$  film. (e) SAED patterns measured after the electroforming process.



Fig. S2 XPS spectra for O1s peaks in (a) the pristine  $WO_3$  and (b) NFA-embedded  $WO_3$  films.



**Fig. S3** Two-probe *I-V* characteristics with contacts the WO<sub>3</sub> film and the conducting ITO substrate. (a, b) The measured *I-V* curves for the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes. The insets show magnified views of the *I-V* curves. (c, d) The resistance as a function of the point number at 0.1 V read voltage. The resistance ratio between the pristine WO<sub>3</sub> and NFA-embedded WO<sub>3</sub> electrodes more than 6 orders of magnitude.



**Fig. S4** (a) Distribution of electroforming voltage for the NFA-embedded WO<sub>3</sub> electrode. The inset shows the electroforming voltage. (b) Retention characteristic of the NFA-embedded WO<sub>3</sub> electrode at room temperature and 0.1 V read voltage with almost stable current value. (c) Cycling performance for 10000 cycles at a scan rate of 150 mV s<sup>-1</sup>. (d) Determination of the *b*-value at scan rates from 5 to 100 mV s<sup>-1</sup>.



Fig. S5 (a) Photograph showing the asymmetric supercapacitor. The galvanostatic charge– discharge profiles of (b) the pristine  $WO_3//C$  and (c) NFA-embedded  $WO_3//C$  asymmetric supercapacitor devices at various current densities.



**Fig. S6** Energy density vs. power density for the pristine  $WO_3//C$  and NFA-embedded  $WO_3//C$  asymmetric supercapacitors.



**Fig. S7** (a, b) Optical modulation and (c) coloration efficiency for the pristine WO<sub>3</sub> and NFAembedded WO<sub>3</sub> electrodes.

Table S1 Percentages of different chemical states of W for pristine  $WO_3$  and NFA-embedded  $WO_3$  films.

	Percentages of chemical states of W (%)					
Chemical states	Pristine WO <sub>3</sub>	NFA-embedded WO <sub>3</sub>				
W <sup>0</sup> (Metallic W)	0	12.3				
$W^{4+}(WO_2)$	0	33.6				
$W^{5+}(W_2O_5)$	32.2	10.9				
$W^{6+}(WO_3)$	67.8	43.2				