Electronic Supplementary Information

Effect of Substrate Pre-treatment on Microstructure and Enhanced Electrochromic Properties of WO$_3$ Nanorod Arrays

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1. Figure S1 showed the XRD pattern of the as-prepared WNRAs grown TiO$_2$ seed layer annealed at 700 °C for 15 min under a hydrothermal process at 180 °C for 8 h. It can be seen that all the diffraction peaks could be well indexed to the standard diffraction pattern of hexagonal phase WO$_3$ (JCPDS 01-075-2187) except for the diffraction peaks indexed to the FTO substrate.

![Figure S1 XRD pattern of the as-prepared WNRAs grown TiO$_2$ seed layer annealed at 700 °C for 15 min under a hydrothermal process at 180 °C for 8 h.]

2. Figure S2 gave the SEM images of A$_{Ti700}$ nanorod arrays before and after the CV

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test. It can be seen from Figure S2 that after cycling test, the shapes and growth orientation of the nanorods in $A_{Ti700}$ didn’t change, which meant the $A_{Ti700}$ nanorod arrays had good structure and cycling stability.

Figure S2 SEM images of $A_{Ti700}$ nanorod arrays (a) before and (b) after CV test
3. Figure S3 illustrated the visible transmittance spectra of the as-prepared TiO$_2$ and WO$_3$ seed layers. It can be seen that the transmittance modulation of the TiO$_2$ seed layer was less than 3% (Transmittance$_\text{at bleached state}$ (85.7%)-Transmittance$_\text{at colored state}$ (82.8%)), while that of the WO$_3$ seed layer was larger than 24% (78.3%-53.8%) at the wavelength of 660 nm.

Figure S3 The visible transmittance spectra of (a) as-prepared TiO$_2$ seed layer annealed at 700 °C for 15 min and (b) WO$_3$ seed layer annealed at 500 °C for three times (10, 10, 30 min) at colored and bleached states when applied -3.0 V and +3.0 V for 100 s, respectively.
4. Figure S4 exhibited the plots of current density vs. time of the $A_{Ti700}$ and $A_{W}$. As for $A_{Ti700}$, the sections of the current density vs. time plot at 100-200 s and 200-300 s corresponded to the coloring and bleaching process, respectively. The current densities could quickly reach their saturation after the voltage switching for both coloring and bleaching process, while, as for $A_{W}$, the current densities were slowly to get to their saturation, especially for the bleaching process. Compared with $A_{W}$, $A_{Ti700}$ showed larger current densities and faster response after the voltage switching, indicating $A_{Ti700}$ was easier for the intercalation/deintercalation of the Li$^+$ ions, thus major transmittance modulations for coloring and bleaching could be completed in shorter time. Moreover, $A_{Ti700}$ showed smaller charge density for the accomplishment of the coloring and bleaching process than $A_{W}$, revealing that a serial of $\Delta OD$ values could be obtained in $A_{Ti700}$ with smaller charge density.

![Figure S4 The plots of current density vs. time of the $A_{Ti700}$ and $A_{W}$.](image)
5. Figure S5 showed the SEM images of the TiO$_2$ seed layer annealed at different temperatures (550-700 °C) and WO$_3$ seed layer. It can be found that the grain sizes of the TiO$_2$ nanoparticles in the seed layers increased with increasing the annealing temperatures (Figure S5 (a)-(c)). According to the statistics from the corresponding SEM images, the average diameters of the TiO$_2$ nanoparticles were about 15.0, 25.0 and 35.0 nm, respectively, and the average grain size of the WO$_3$ seeds was about 37.5 nm.

Figure S5 SEM images of the TiO$_2$ seed layers annealed at (a) 550 °C for 30 min, (b) 650 °C for 30 min and (c) 700 °C for 15 min and (d) WO$_3$ seed layer annealed at 500 °C.
6. The EIS of A\textsubscript{W} and A\textsubscript{Ti700} nanorod arrays were tested and the results were shown in Figure S6. The EIS tests were carried out by applying an AC voltage of 10 mV in the frequency range 100 kHz to 0.01 Hz at their bleached states. A Randles circuit model was used to fit data presented in the inset of Figure S6. The Randles circuit model comprised of series resistance (Rs) of the system (resulting from electrolyte/substrate resistance), Rct the charge transfer resistance (i.e. interfacial redox reaction resistance) connected in parallel with an electrical double layer capacitance (Cdl) at the electrolyte/electrode interface and finally the Warburg diffusion element (Zw) accounting from the ionic diffusion and charging of film. These parameters could be calculated by using ZSimpwin software (Table S1). From Table S1 it is known that the values of Rs, Rct and Zw of the A\textsubscript{Ti700} were all smaller than those of A\textsubscript{W}, further confirming the fast charge transfer which finally led to shorter switching time and higher coloration efficiency of the A\textsubscript{Ti700}.

![Figure S6 EIS of A\textsubscript{W} (black) and A\textsubscript{Ti700} (red)](image)

Table S1 EIS parameters of A\textsubscript{Ti700} and A\textsubscript{W} obtained by fitting the data to Randles circuit.

<table>
<thead>
<tr>
<th></th>
<th>Rs (Ω)</th>
<th>Rct (Ω)</th>
<th>Zw (S s\textsuperscript{1/2}cm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{W}</td>
<td>77.2</td>
<td>487.7</td>
<td>0.04</td>
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<tr>
<td>A\textsubscript{Ti700}</td>
<td>5.5</td>
<td>194.5</td>
<td>0.03</td>
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