

Supplemental Information:

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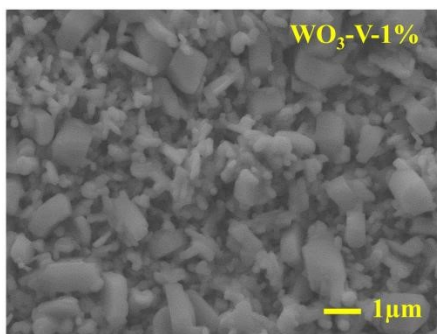


Fig. S1. SEM images of $\text{WO}_3\text{-V-1\%}$

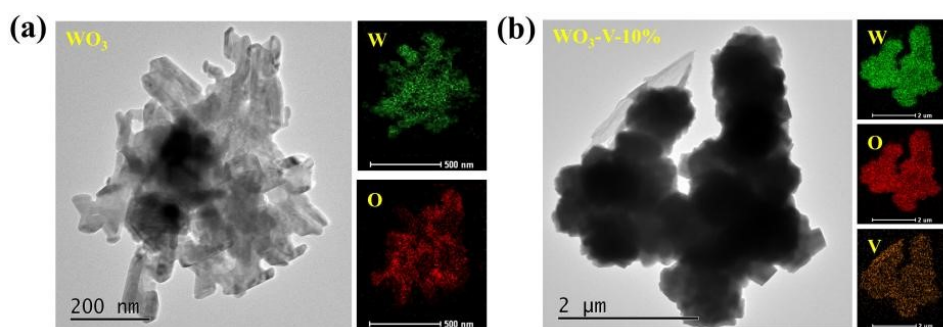


Fig. S2. TEM images and corresponding EDX elemental mapping images of (a) WO_3 and (b) $\text{WO}_3\text{-V-10\%}$

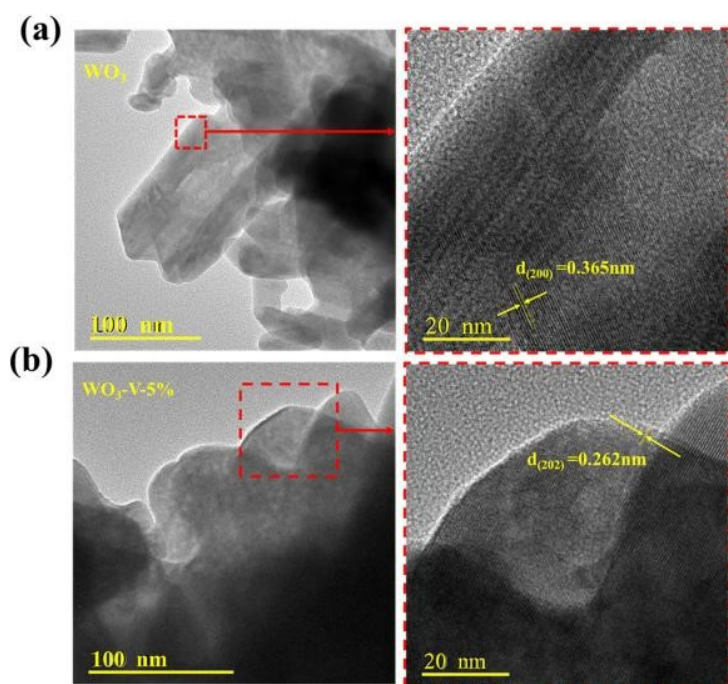


Fig. S3. TEM images of (a) WO_3 and (b) $\text{WO}_3\text{-V-5\%}$ and the corresponding HRTEM images

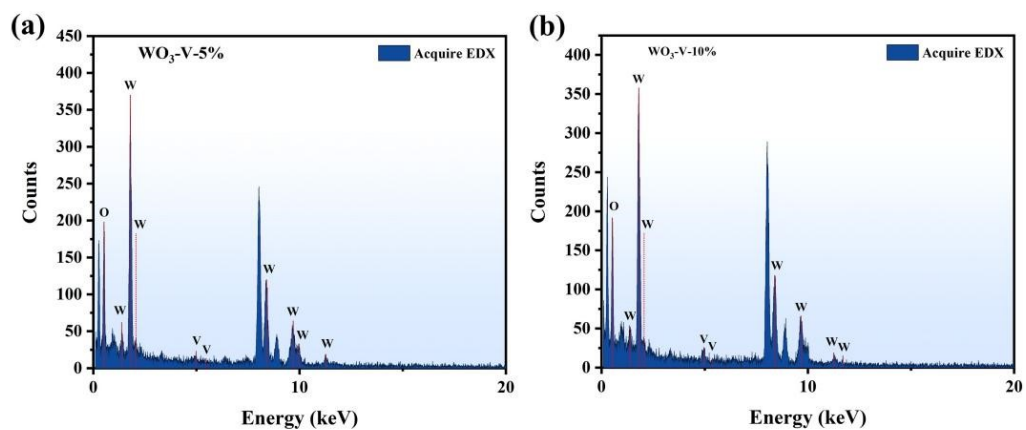


Fig. S4. EDS of W, O and V in (a) $\text{WO}_3\text{-V-5\%}$ and (a) $\text{WO}_3\text{-V-10\%}$ films

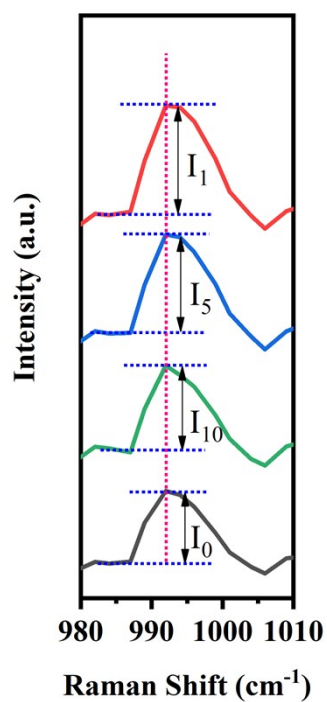


Fig. S5. Localized Raman spectra of WO_3 (black line), $\text{WO}_3\text{-V-1\%}$ (red line), $\text{WO}_3\text{-V-5\%}$ (blue line) and $\text{WO}_3\text{-V-10\%}$ (green line) films

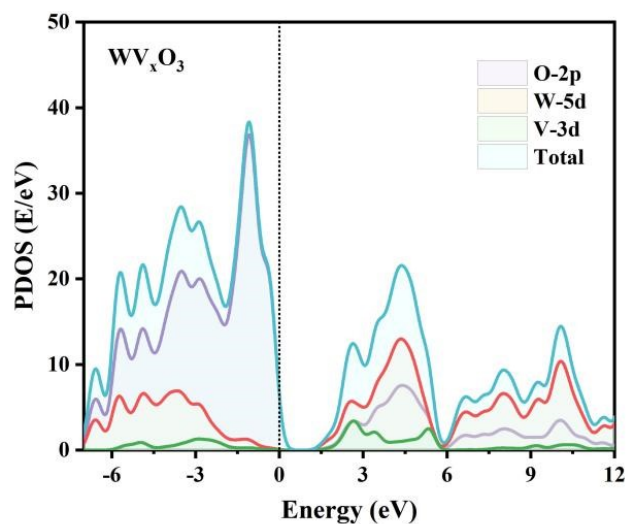


Fig. S6. PDOS patterns of W 5d , O 2p and V 3d orbitals for WV_xO_3

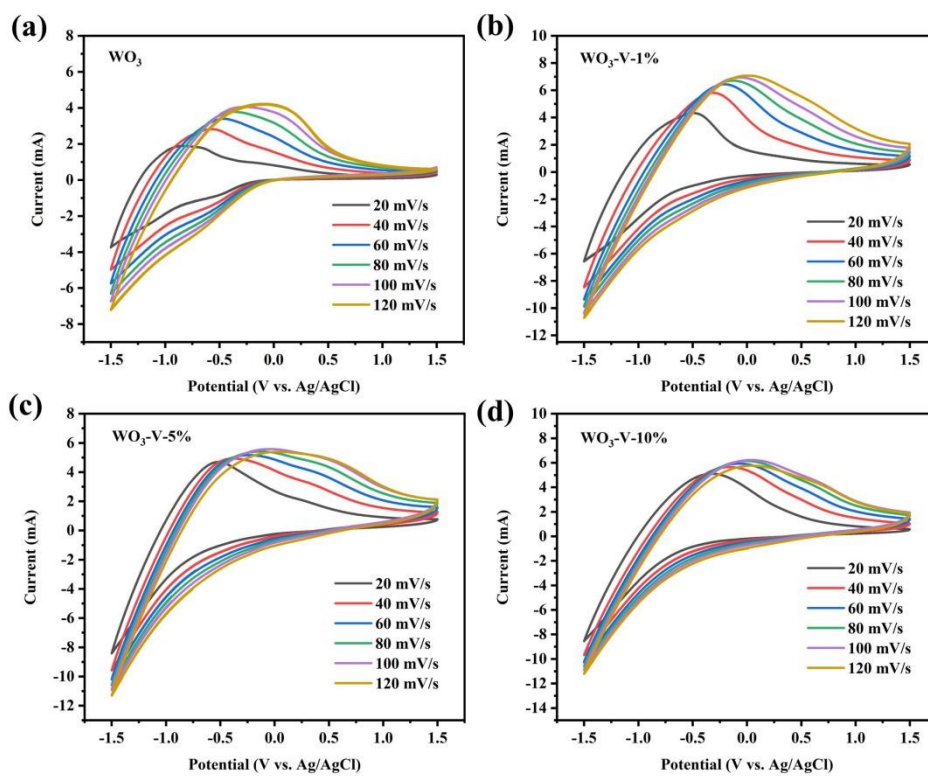


Fig. S7. CV curves for (a) WO_3 , (b) $WO_3-V-1\%$, (c) $WO_3-V-5\%$ and (d) $WO_3-V-10\%$ with various scan rates

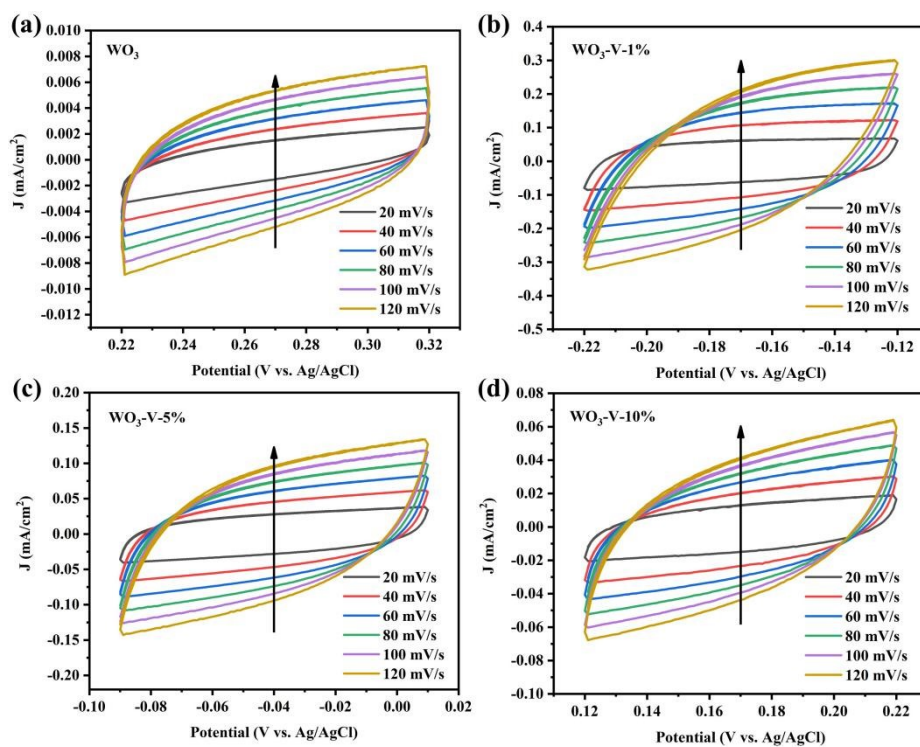


Fig. S8. CV curves for (a) WO_3 , (b) WO_3 -V-1%, (c) WO_3 -V-5% and (d) WO_3 -V-10% in the region of OCP \pm 50 mV (V vs. Ag/AgCl) with various scan rates

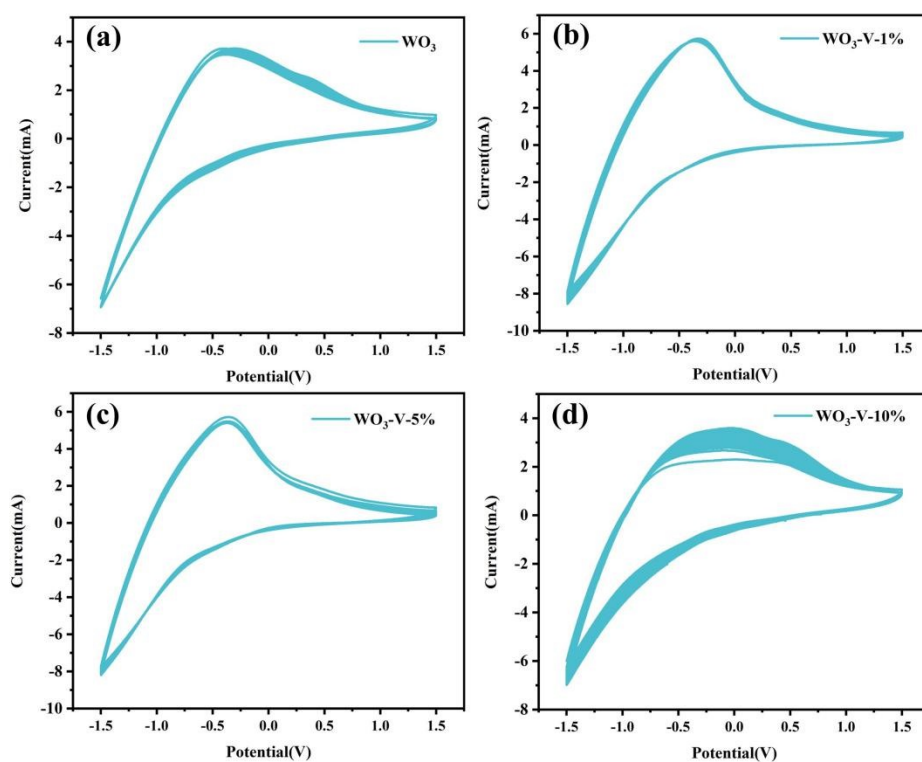
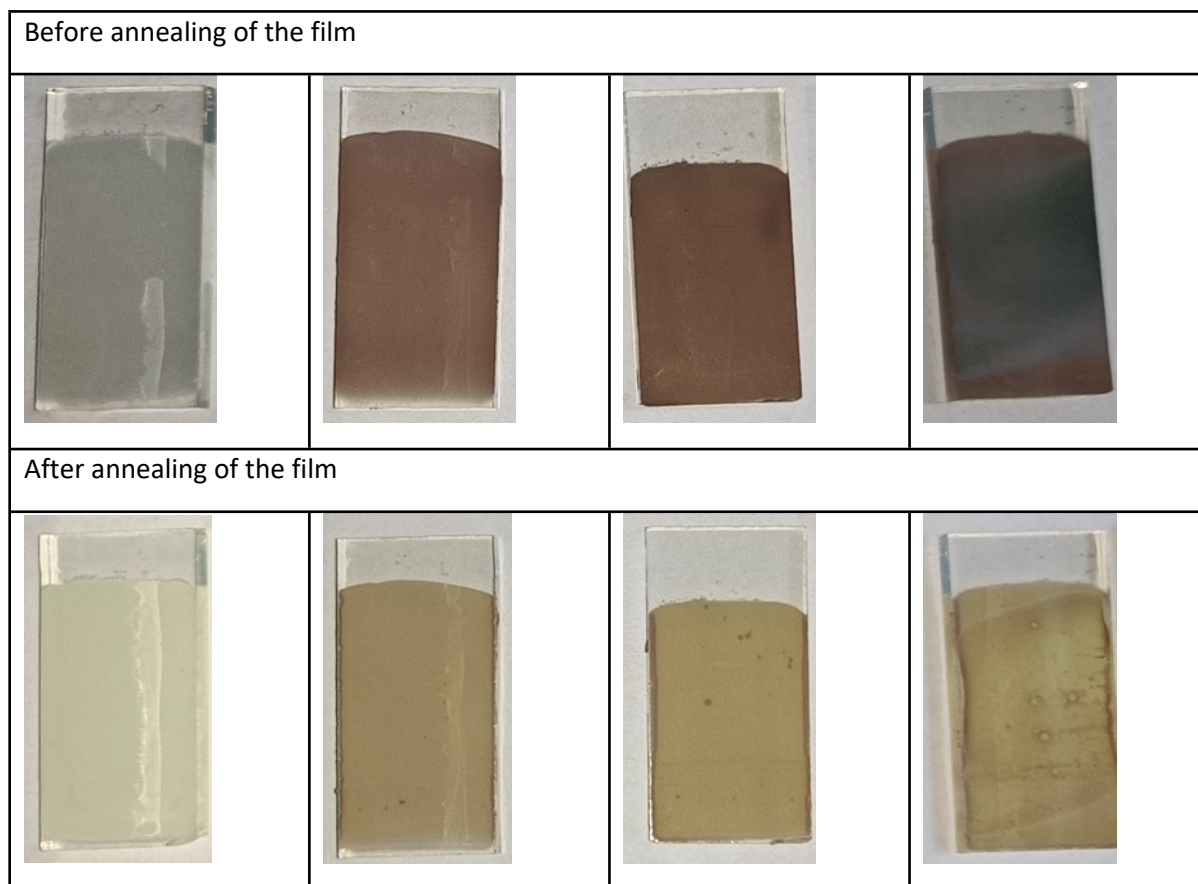


Fig. S9. After 50 times cycle CV curves of (a) WO_3 , (b) WO_3 -V-1%, (c) WO_3 -V-5% and (d) WO_3 -V-10%

Tab. S1. Comparison of pictures of films before and after annealing



Tab. S2. EDS elemental mapping of O, V and W in V-doped WO_3 thin films of different concentrations

| Element | WO_3 | WO_3 -V-1% | WO_3 -V-5% | WO_3 -V-10% |
|---------|--------|--------------|--------------|---------------|
| O(K) | 66.99 | 73.31 | 78.91 | 84.33 |
| V(K) | 0.00 | 0.12 | 0.80 | 1.93 |
| W(L) | 33.01 | 26.57 | 20.29 | 13.74 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |

Tab. S3. Percentage XPS atoms of W, C,V and O in V-doped WO_3 thin films of different concentrations

| Name | WO ₃ | WO ₃ -V-1% | WO ₃ -V-5% | WO ₃ -V-10% |
|------|-----------------|-----------------------|-----------------------|------------------------|
| W4f | 14.97 | 25.77 | 23.94 | 21.9 |
| C1s | 15.9 | 15.92 | 14.73 | 16.37 |
| V2p | 0.00 | 0.67 | 2.07 | 4.64 |
| O1s | 69.13 | 57.64 | 59.25 | 57.09 |

Tab. S4. Crystal size of WO₃, WO₃-V-1%, WO₃-V-5% and WO₃-V-10% films

| Name | Crystal Surface | 2θ (°) | Cos θ | FWHM | D (nm) | Average D (nm) |
|------------------------|-----------------|--------|-------|-------|--------|----------------|
| WO ₃ | (200) | 24.334 | 0.978 | 0.188 | 42.855 | 39.055 |
| | (020) | 23.560 | 0.979 | 0.222 | 36.177 | |
| | (002) | 23.101 | 0.980 | 0.210 | 38.132 | |
| WO ₃ -V-1% | (200) | 24.319 | 0.978 | 0.194 | 41.503 | 46.564 |
| | (020) | 23.570 | 0.979 | 0.148 | 54.511 | |
| | (002) | 23.087 | 0.980 | 0.184 | 43.677 | |
| WO ₃ -V-5% | (200) | 24.349 | 0.978 | 0.211 | 38.167 | 41.029 |
| | (020) | 23.617 | 0.979 | 0.178 | 45.203 | |
| | (002) | 23.102 | 0.980 | 0.202 | 39.717 | |
| WO ₃ -V-10% | (200) | 24.391 | 0.977 | 0.170 | 47.323 | 47.781 |
| | (020) | 23.644 | 0.979 | 0.162 | 49.408 | |
| | (002) | 23.148 | 0.980 | 0.172 | 46.612 | |

Microstress and microstrain in WO₃, WO₃-V-1%, WO₃-V-5% and WO₃-V-10% films

| Name | 2θ (°) | β (°) | D (nm) | $\delta \times 10^{-3} (\text{nm}^{-2})$ | Average stress | $\epsilon \times 10^{-3}$ | Average strain |
|-----------------------|--------|-------|--------|--|----------------|---------------------------|----------------|
| WO ₃ | 24.334 | 0.003 | 42.855 | 0.545 | 0.666 | 3.795 | 4.309 |
| | 23.560 | 0.004 | 36.177 | 0.764 | | 4.641 | |
| | 23.101 | 0.004 | 38.132 | 0.688 | | 4.490 | |
| WO ₃ -V-1% | 24.319 | 0.003 | 41.503 | 0.581 | 0.481 | 3.921 | 3.641 |
| | 23.570 | 0.003 | 54.511 | 0.337 | | 3.079 | |

| | | | | | | | |
|------------------------|--------|-------|--------|-------|-------|-------|-------|
| | 23.087 | 0.003 | 43.677 | 0.524 | | 3.922 | |
| | 24.349 | 0.004 | 38.167 | 0.686 | | 4.259 | |
| WO ₃ -V-5% | 23.617 | 0.003 | 45.203 | 0.489 | 0.603 | 3.706 | 4.092 |
| | 23.102 | 0.004 | 39.717 | 0.634 | | 4.310 | |
| | 24.391 | 0.003 | 47.323 | 0.447 | | 3.429 | |
| WO ₃ -V-10% | 23.644 | 0.003 | 49.408 | 0.410 | 0.439 | 3.386 | 3.493 |
| | 23.148 | 0.003 | 46.612 | 0.460 | | 3.665 | |

1. Grain Size Calculation

Crystal size is a measure of the size of the grains in a material and has an important effect on the properties and stability of the material. Doping of V usually results in a small change in the crystal lattice constant. This change may be caused by V substituting or occupying vacancies with tungsten atoms in WO₃ crystals. The Debye-Scherrer formula can be used to calculate the grain size.

$$D = K\lambda / (\beta \cos\theta) \quad (1)$$

Where D is the grain size (nm), K is a constant taken as 0.89, λ is the X-ray wavelength, which is taken as 0.15406 nm for Cu- α , β is the half-peak width of the diffraction peak and θ is the angle of diffraction. The formula is based on the relationship between the half-height width of the diffraction peak and the grain size, and the grain size can be calculated by measuring the half-height width of the diffraction peak. Combining the coefficients in the formula, grain sizes of 39.055 nm, 46.564 nm, 41.029 nm, and 47.781 nm can be obtained for WO₃, WO₃-V-1%, WO₃-V-5% and WO₃-V-10%, respectively.

Different concentrations of vanadium ions may introduce different kinetics of nucleation growth and lattice diffusion during crystal growth, leading to changes in grain size. Vanadium enters the WO₃ lattice as an impurity and may affect the processes of nucleation and crystal growth. The presence of vanadium may reduce the energy of the grain boundaries during the crystal growth process, which promotes the formation and growth of nuclei, leading to an increase in grain size. A large grain size can reduce the number of grain boundaries and decrease the defect density of the material, which helps to improve the stability and consistency of the optical properties. In addition, larger grain sizes result in shorter response times and may increase conductivity or decrease electrical resistance, which may be more advantageous for applications that require rapid color change or transmittance in the presence of an electric field. Electrochemical testing also reflects faster response times and significantly lower resistivity with V doping. Tab. S4 is about the grain size in WO₃, WO₃-V-1%, WO₃-V-5% and WO₃-V-10% films (The selected XRD peaks are the three strongest peaks). The grain sizes in the WO₃-V-1% and WO₃-V-10% films are relatively large, but in conjunction with the corresponding SEM, the WO₃-V-10% has more pronounced clusters, which is unfavorable for ion and electron transport.

The reduction of stress can reduce the deformation and stress concentration of the material under the action of electric field, which can help to improve the stability and reliability of the material, thus improving the effect and durability of electrochromic change. Stress reduction can reduce the risk of fatigue damage of the material under electric field loading and extend the service life and durability of electrochromic materials. This is especially important for application scenarios where long-term stability is required. Tab. S5 is about microstress and microstrain in WO₃, WO₃-V-1%, WO₃-V-5% and

WO₃-V-10% films (2θ is peak position and β is its corresponding FWHM. δ (nm⁻²) is the dislocation density, and its value is calculated using the formula $\delta = 1/D^2$. ϵ is the microstrain, and it is calculated using the formula $\epsilon = \beta/4\tan\theta$). It can be concluded from Tab. S4-S5 that as the doping concentration increases, the WO₃ particle size becomes larger and then smaller, while the microstress present inside becomes smaller and then larger. When the concentration reaches 10% the particle size becomes larger again and the microstress decreases again. This may be due to the high doping concentration of 10%, which leads to the lattice collapse, the internal microstress decreases, the particles bond together and form larger grains, resulting in lower porosity and lower reactivity of the material. Therefore, the WO₃-V-10% films show lower electrochemical activity. At the same time, it can be macroscopically seen that the WO₃-V-10% samples show uneven discoloration before and after discoloration.

2. Charge density calculation

The charge density calculation can be seen in Eq:

$$Q = S/(VA) \quad (2)$$

Where Q represents the charge density (C/cm²), S is the area enclosed by the cyclic voltammogram curve, V is the scan rate (V/s), and A is the surface area of the working electrode (cm²) [43].

3. Peak current value calculation

The peak current value (i_p) can be calculated using the equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C V^{1/2} \quad (3)$$

Where i_p represents the peak current value, n is the number of electrons involved in the electrochemical reaction (assumed to be 1), A is the electrode area of the film, D is the Li⁺ diffusion coefficient, C is the ion concentration of Li⁺, and V is the scan rate [44].

4. Calculation of transmittance difference

The calculation formula is as follows:

$$\Delta T = (T_b - T_c) \quad (4)$$

Where T_b and T_c represent the transmittance of the sample under bleached and colored conditions, respectively, at a certain wavelength.

5. CE calculation

To further determine the coloring efficiency of the prepared samples, the following formula can be utilized:

$$CE = \Delta OD/Q_i \quad (5)$$

$$\Delta OD = \log (T_b/T_c) \quad (6)$$

Where CE represents the coloration efficiency (cm²/C); ΔOD indicates the maximum change in optical density; Q_i is the quantity of charge injected or extracted per unit area. T_b and T_c are the transmittances in the bleached and colored states, respectively.