Electronic Supplementary Information (ESI)

Vertically aligned 3D-hierarchical flower like WO_3 nanoarray films with highly enhanced electrochromic performance†

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S1. FESEM IMAGES

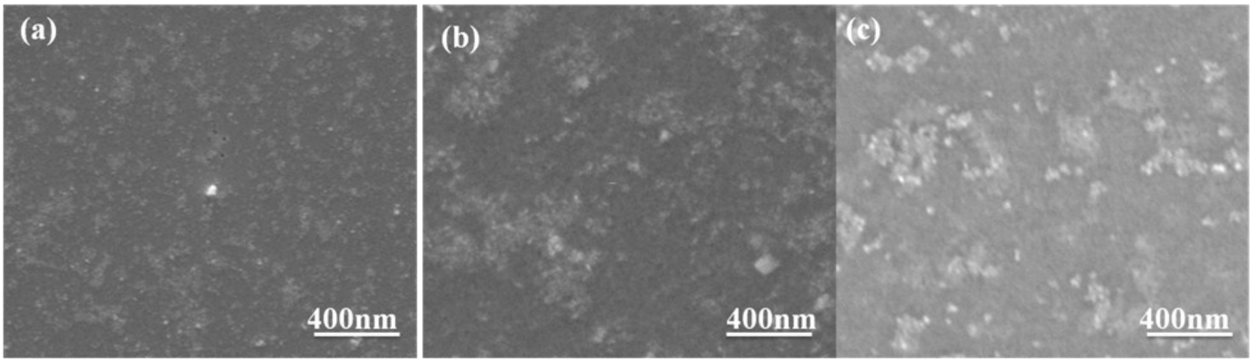

Fig.S1 FESEM images of the as-deposited WO_3 thin films (a) W1, (b) W3 and (c) W3.

S2. XRD Pattern

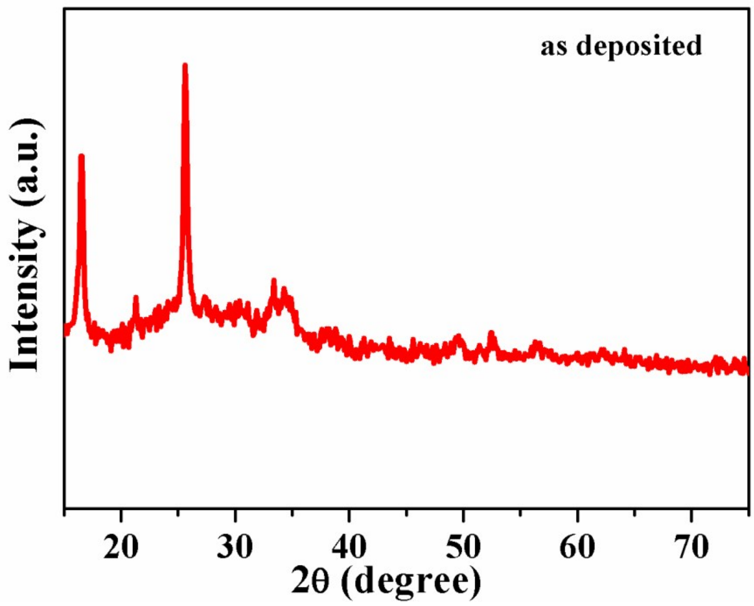

Fig.S2 XRD pattern of the as deposited WO_3 thin film.

S3. Cross section FESEM image

The thickness values of electrodeposited WO_3 thin films were determined from the cross sectional FESEM images. The average thickness for W1, W2 and W3 film is 501.2 nm, 595.5 nm, 976.3 nm respectively.

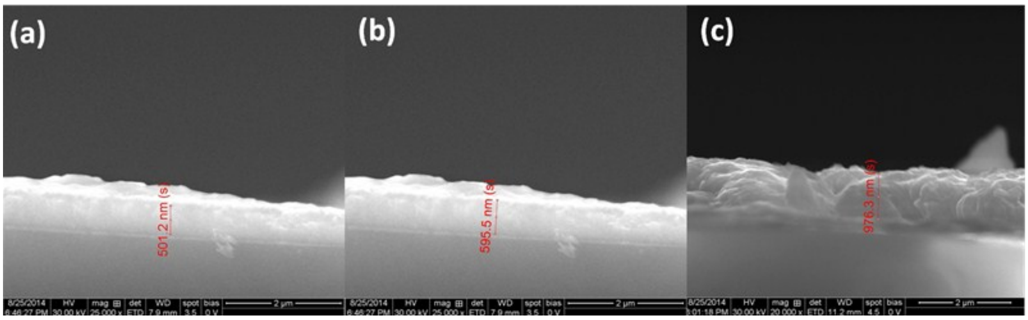

Fig.S3 The cross section FESEM images of WO_3 thin film (a) W1, (b) W2 and (c) W3.

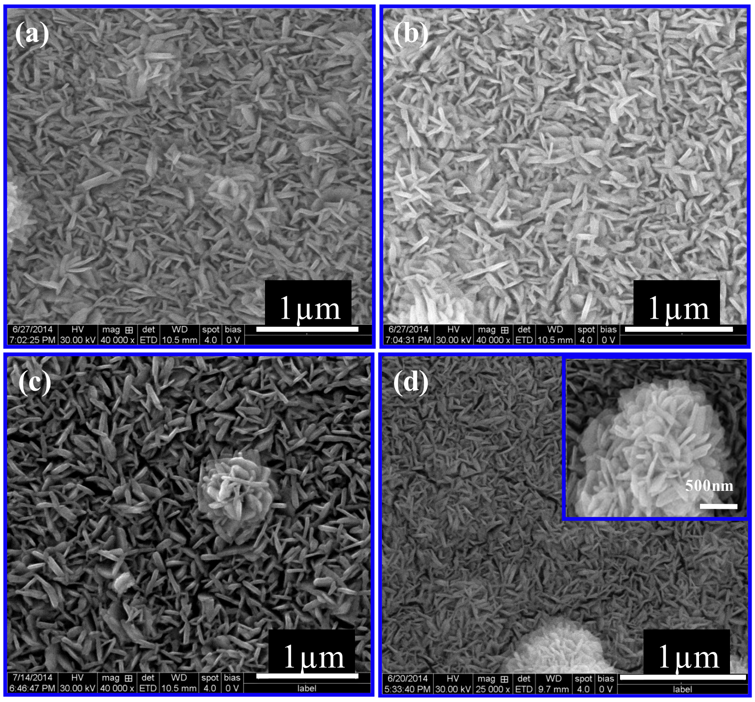

Fig.S4 FESEM images of the WO_3 thin film (W2) with different deposition time (a) 10 min, (b) 20 min, (c) 30 min, (d) 45 min.

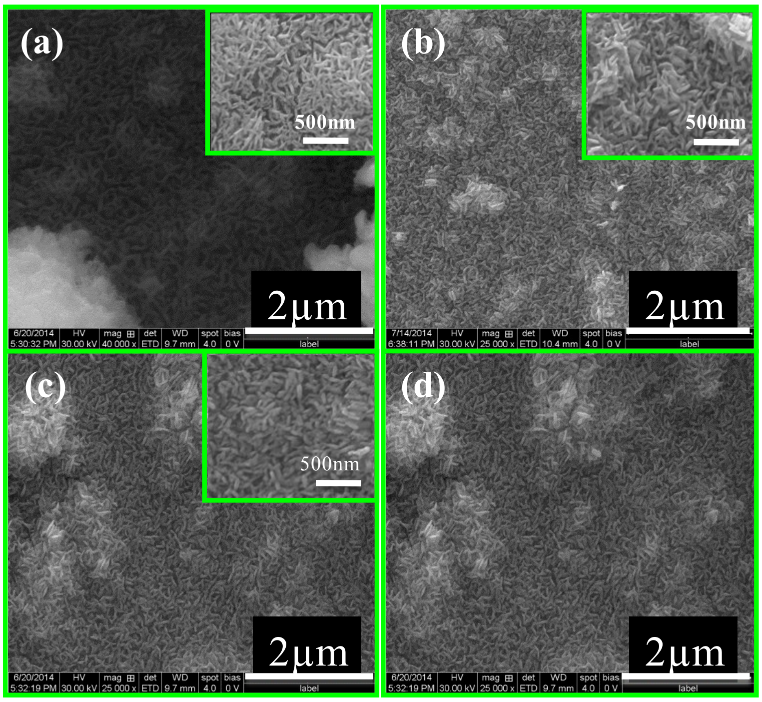

Fig.S5 FESEM images of the WO_3 thin film (W1) with different deposition time (a) 10 min, (b) 20 min, (c) 30 min, (d) 45 min.

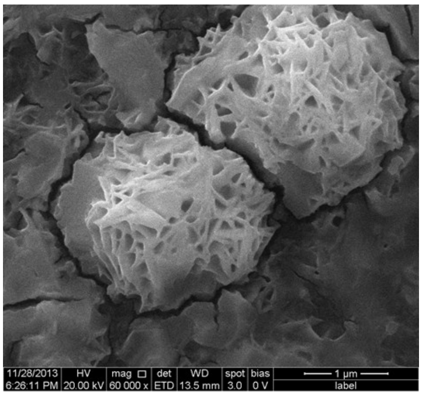

Fig.S6 FESEM images ofelctrodeposited WO_3 thin film in the absence of organic acid like oxalic acid.

S7. Bandgap calculation

The optical band gaps of these films can be estimated from the absorption coefficient by using the Tauc equation,[1]

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (1)$$

Depending on the optical transition, the exponential n takes the value 2 for direct allowed transition and 1/2 for indirect allowed transition. Since the WO_3 is an indirect bandgap semiconductor, bandgap energies of all the thin films have been estimated by plotting $(\alpha h\nu)^{1/2}$ as a function of the photon energy hυ. The optical bandgap values for the three samples are found to be 2.82, 2.51 and 2.47 eV for W1, W2 and W3 respectively which are shown in Fig.S7.

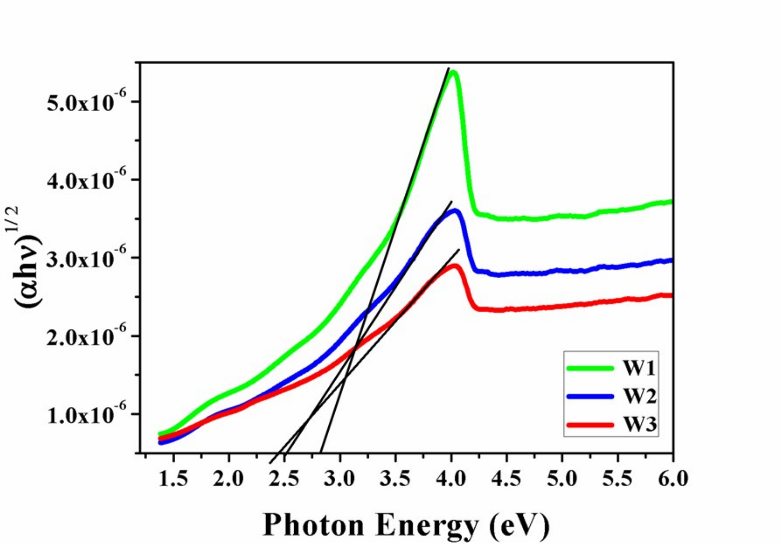

Fig.S7 Tauc plot from which bandgap of the WO_3 thin films are estimated.

S8. Method of calculation of optical constants

From optical reflectance measurements of the electrodeposited WO_3 films, refractive index n and extinction coefficient k have been calculated as a function of the wavelength in the visible region using Fresnel formula. The complex refractive index for the films is expressed by, N = n− ik. According to the Fresnel formula, the reflectance R can be expressed as a function of the refractive index n and the absorption index k:[2]

$$R' = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad (2)$$

Where the extinction coefficient is obtained by using k = αλ / 4π. The absorption coefficient α is evaluated from the experimental spectra of transmittance T (λ) and reflectance R (λ) using the following expression (3):[3]

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right] \qquad (3)$$

Therefore by evaluating the values of α and k, the refractive index of the film can be obtained from (4)

$$n = \left(\frac{1+R'}{1-R'}\right) + \sqrt{\frac{4R'}{(1-R')^2} - k^2} \qquad (4)$$

Fig.S8 shows the refractive indices of the nanospindles (W1), nanoplatelets (W2) and hierarchical flower like architectures (W3) films. The average refractive indices of W1, W2 and W3 films at 550nm are 2.30, 2.15, and 1.90 respectively in the visible range of about 300 to 900nm.

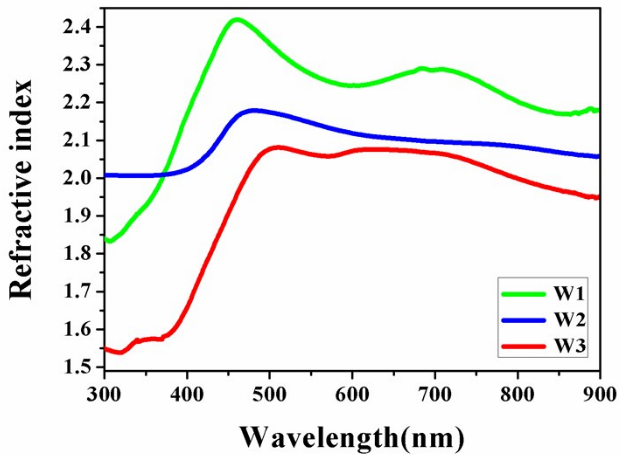

Fig.S8 Refractive indices of WO_3 thin films (W1, W2 and W3).

S9. Porosity Calculation

The refractive index of WO_3 thin films is significantly related to the porosity of the films by the following expression,[4]

$$Porosity(\%) = \left(1 - \frac{n_{film}^2 - 1}{n_b^2 - 1}\right) \times 100 \tag{5}$$

where n_{film} is the refractive index of the film, and n_b is the refractive index of the bulk WO_3. By substituting the values of refractive index of each film, the porosity values of the W1, W2 and W3 were calculated as shown in Table 1(**Fig. S13**).

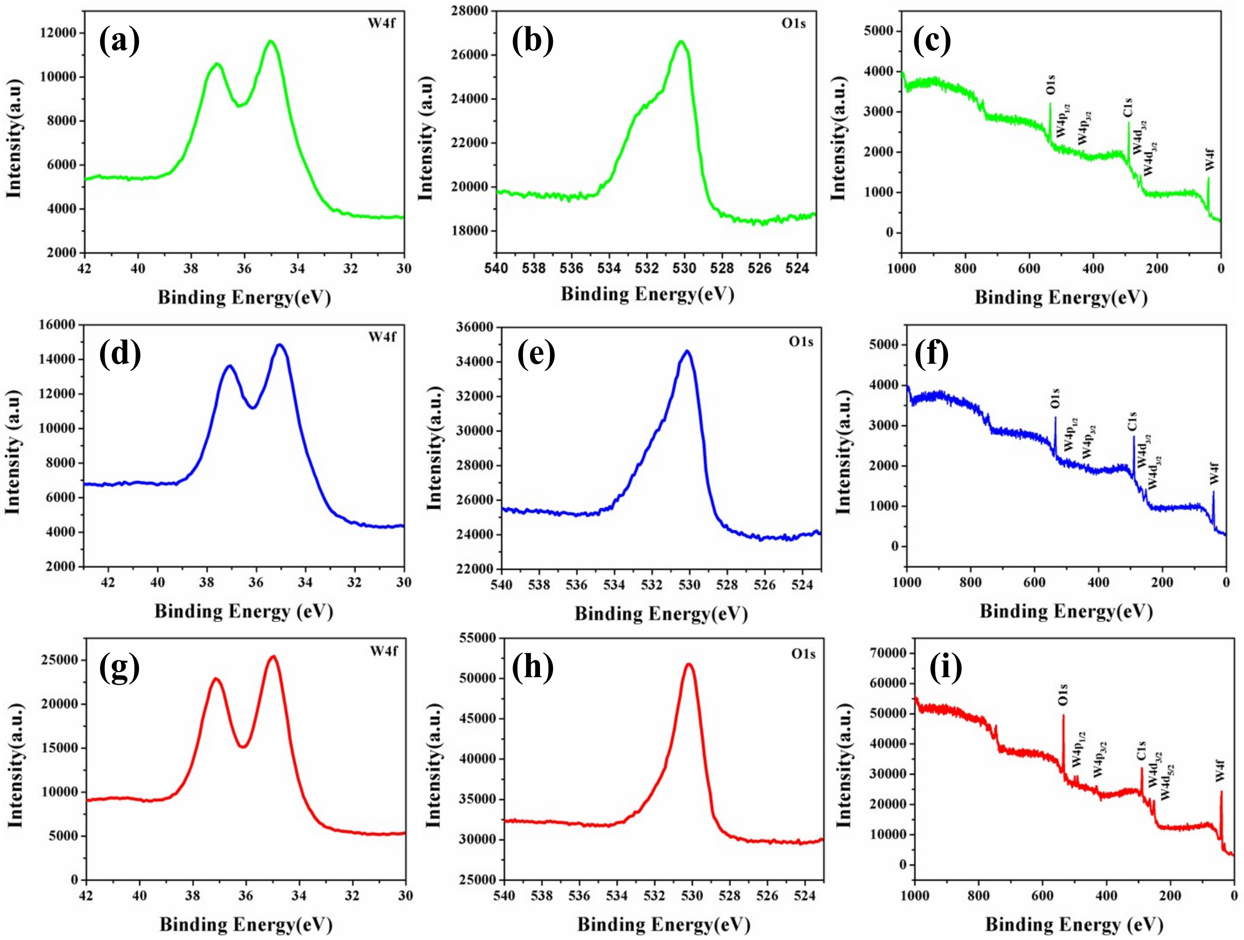

Fig.S10 XPS W4f, O1s, and wide angle spectra of the electrodeposited WO_3 thin films: (a-c) Nanospindles (W1), (d-f) Nanoplatelets (W2), (g-i) Hierarchical flower (W3). (The O1s spectra show the main peak at 530.2 eV. A couple of bands located at 37.1 eV and 35.0 eV corresponds to the $W4f_{5/2}$ and $W4f_{7/2}$ signals).

S11. Diffusion coefficient calculation

From the CV plots (Fig. 10(a)), by using the values of cathodic and anodic peak currents, the diffusion coefficient (D) of H^+ ions in the electrode during intercalation and deintercalation were calculated using the RandlesSevcik equation,

$$D = \frac{i_p}{2.72 \times 10^5 \times n^{3/2} \times A \times C_0 \times \upsilon^{1/2}} \quad (6)$$

where D is the diffusion coefficient of H^+ ions, i_p is the peak current density, n is the number of electrons involved in the redox process (n=1 for W^{5+} / W^{6+} redox pair), A is the area of the film, C_o is the concentration of active ions in the electrolyte and υ is the potential scan rate. The values of diffusion coefficient calculated for the H^+ ion in the WO_3 films are listed in Table 1(Fig. S13†). The calculated diffusion coefficients of W1, W2 and W3 were 4.9068×10^{-7}, 6.792×10^{-7}, 1.847×10^{-6} cm^2/s(intercalation) and 2.931×10^{-7}, 3.7892×10^{-7} and 7.196×10^{-7} cm^2/s (deintercalation) respectively.

S12. Coloration efficiency calculation:

The coloration efficiency (CE or η) is one of the important factors to characterize the intrinsic performance of electrochromic materials. The change in optical density (ΔOD) per unit of charge density intercalated into the electrode material during switching is termed as coloration efficiency. It can be determined using the following equation (7)

$$CE or \eta = \frac{\Delta OD}{Q_i/A} \quad (7)$$

where ΔOD is the optical density change measured at a wavelength of 550 nm, Q_i is the amount of charge intercalated into the WO_3 film electrode and A is the area of the film electrode. From Fig. 12, by using the values of T_b and T_c, the change in optical density (ΔOD) of WO_3 film at 550 nm, is determined by the following equation:[5]

$$\Delta OD = \log(\frac{T_b}{T_c}) \quad (8)$$

The calculated coloration efficiencies for W1, W2 and W3 film electrodes are found to be 59.34 $cm^2\ C^{1}$, 142.83 $cm^2\ C^{-1}$ and 172.08 $cm^2\ C^{-1}$ respectively.

S13. Table 1

sample	Transmittance (%)		Optical density ΔOD	Reversibility (%)	Response time (s)		Diffusion coefficient (cm^2s^{-1})		Coloration efficiency (cm^2C^{-1})	Porosity (%)
	Bleached	Colored			t_b	t_c	Intercalation	Deintercalation		
W1	61.50	33.88	0.258	47.24	3.38	6.88	4.906×10^{-7}	2.931×10^{-7}	59.34	18.28
W2	68.52	6.99	0.991	87.86	4.12	7.10	6.792×10^{-7}	3.789×10^{-7}	142.83	31.01
W3	79.90	2.36	1.529	94.11	3.82	5.50	1.847×10^{-6}	7.196×10^{-7}	172.08	50.28

Fig.S13 Electrochromic parameters of different WO_3 nanostructured thin films.

References:

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2. D. T. Phan, A. A. M. Farag, F. Yakuphanoglu, G. S. Chung, *J Electroceram.* 2012, **29**, 12.
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4. G. M. Wu, T. H. Yang, J. Wang and J. Shen, *Atomic Energy Sci. Technol. 1999,* **33**, 332.
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