Supporting Information

The pure inorganic multi-color electrochromic thin films: vanadium-substituted Dawson type polyoxometalates based electrochromic thin films with tunable colors from transparent to blue and purple

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Fig. S1. The TG analysis of the (a) $\alpha_2$-P$_2$W$_{17}$V, (b) $\alpha$-P$_2$W$_{16}$V$_2$ and (c) $\alpha$-P$_2$W$_{15}$V$_3$.

Fig. S2. The cyclic voltammograms during preparing (a) $\alpha_2$-P$_2$W$_{17}$V, (b) $\alpha$-P$_2$W$_{16}$V$_2$ and (c) $\alpha$-P$_2$W$_{15}$V$_3$-based composite films.

Fig. S3. The 200 cycles of CV test of the (a) $\alpha_2$-P$_2$W$_{17}$V-, (b) $\alpha$-P$_2$W$_{16}$V$_2$- and (c) $\alpha$-P$_2$W$_{15}$V$_3$-based EC films in HCl (0.1 M) solution.
**Fig. S4.** The IR spectra of the TiO$_2$ substrate (a), the $\alpha$-K$_7$[P$_2$W$_{16}$V$_2$O$_{62}$]$\cdot$18H$_2$O (b) and the composite film (c).

**Fig. S5.** The IR spectra of the TiO$_2$ substrate (a), the $\alpha$-K$_7$[P$_2$W$_{15}$V$_3$O$_{62}$]$\cdot$18H$_2$O (b) and the composite film (c).
Fig. S6. The SEM pictures of the TiO$_2$ substrate.

Fig. S7. (a) The 2D AFM results of the TiO$_2$ substrate; (b) The 3D AFM results of the TiO$_2$ substrate.

Fig. S8. The AFM results of the (a) $\alpha_2$-$P_2W_{17}V$-based composite film, (b) the $\alpha$-$P_2W_{16}V_2$-based composite film and (c) the $\alpha$-$P_2W_{15}V_3$-based composite film.
**Fig. S9.** The photographs of the as-prepared TiO$_2$ substrate (a) and the TiO$_2$ substrate after deposit with $\alpha_2$-$P_2W_{17}V$ (b), $\alpha$-$P_2W_{16}V_2$ (c) and $\alpha$-$P_2W_{15}V_3$ (d).

**Fig. S10.** Cyclic voltammograms (CVs) at different scan rates ($10$, $25$, $50$, $75$, $100$, $125$ and $175$ mV s$^{-1}$) of the TiO$_2$ film deposit with $\alpha$-$P_2W_{16}V_2$-based EC film in HCl (0.1M) solution. Inset: plots of peak current versus the square root of scan rate.
**Fig. S11.** Visible spectra and of the $\alpha$-P$_2$W$_{16}$V$_2$-based EC film under different potentials ranging from -0.5 to -1.6 V.

**Fig. S12.** Potential (a), current (b) and transmittance (c) at 565 nm of the $\alpha_2$-P$_2$W$_{17}$V-based EC film during the subsequent double-potential step chronoamperometric of -1.7~+1.5 V.
Fig. S13. Potential (a), current (b) and transmittance (c) at 590 nm of the α-P$_2$W$_{16}$V$_2$-based EC film during the subsequent double-potential step chronoamperometric of -1.6~+1.3 V.

Fig. S14. The stability and reversibility of the (a) α$_2$-K$_7$[P$_2$W$_{17}$VO$_{62}$]·18H$_2$O-based EC film, (b) the α-K$_8$[P$_2$W$_{16}$V$_2$O$_{62}$]·18H$_2$O-based EC film and (c) the α-K$_9$[P$_2$W$_{15}$V$_3$O$_{62}$]·18H$_2$O-based EC film. The black line represents the first 5 cycles of the double-potential steps; the red dash line represents the 1000$^{th}$ 5 cycles of the double-potential steps.