Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Supporting informations

A new electrodeposit approach for preparing polyoxometalates-based electrochromic smart windows

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Experimental

Materials: $(NH_4)_{14}[NaP_5W_{30}O_{110}]\cdot 31H_2O$ and $Na_9[NaS_5W_{30}O_{110}]\cdot 25H_2O$ were prepared according to literature procedures.[a,b] The TiO_2 paste with particle size of 18nm was bought from Dyesol. FTO glass (14 Ω/□, Nippon Sheet Glass) was purchased from Heptachroma (Dalian, China). The electrolyte is 0.1M LiI in propylene carbonate. The other reagents were all purchased from purchased from Aladdin.

Instruments: Electrochemical experiments were performed on CS350 electrochemistry station (CH Instruments, Wuhan CorrTest® Instrument Corporation, China). X-ray photoelectron spectra (XPS) analyses were performed on a VG ESCALABMKII spectrometer with an Mg-Ka (1253.6 eV) achromatic X-ray source. Scanning electron microscope (SEM, JEOL JSM-840 operated at 20 kV). Atomic force microscopy (AFM) measurements were performed in air with a SPI3800N Probe Station. Visible light absorption spectra and transmittance spectra were obtained with a Varian Cary 500 UV-vis NIR spectrometer. Raman scattering spectra were carried out on Jobin-Yvon HR800 Raman spectrometer with an Ar^+ laser source of 488 nm wavelength in a macroscopic configuration.

Preparation of the EC electrode: The TiO_2 film was prepared using the screen printing method. Print twice to obtain a film with the thickness of ca.4μm. The electrodeposition process is as follows: the counter electrode is Pt wire; the reference electrode is Ag/AgCl and the TiO_2 film acts as working electrode. The TiO_2 film was immersed in the X_5W_{30} (X=P, S) aqueous solution (pH=2.0 0.7mM), then scanned using cyclic voltammogram method between -1.0 and 0.3V at a scan rate of 100 mV s^{-1} for 30 cycles. After that, the film was rinsed with deionized water and dried with hot air, then the film was placed in the oven heat to 150 ^oC for 30min.

Assemble of the EC smart window: A bare FTO with a hole act as the counter electrode. The device was sealed with Surlyn film (45μm) the electrolyte was injected from the hole of the FTO. The hole was sealed with another thin glass.

a I. Creaser, M. C. Heckel, R. J. Neitz, M. T. Pope, *Inorg. Chem.* 1993, **32**, 1573.

b Z.M. Zhang, S. Yao, Y.G. Li, X.B. Han, Z.M. Su, Z.S. Wang, E.B. Wang, Chem. Eur. J. 2012, 18, 9184.

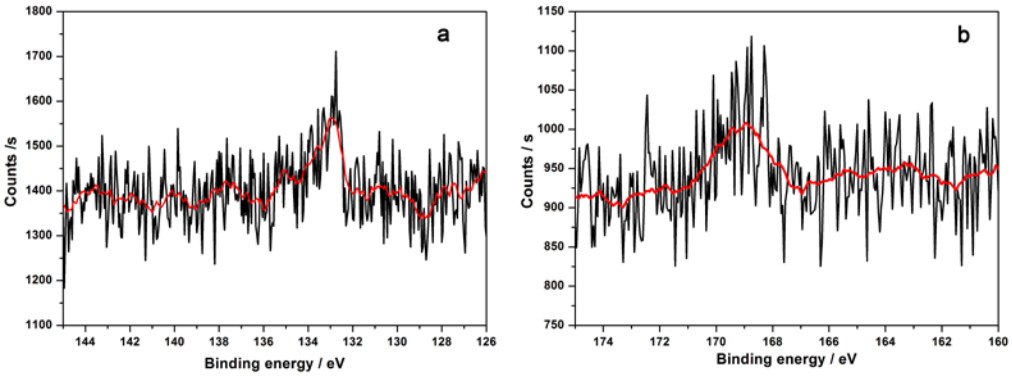

Figure S1 The XPS spectrum of P atom in the P_5W_{30} based EC electrode (a) and the XPS spectrum of S atom in the S_5W_{30} based EC electrode (b).

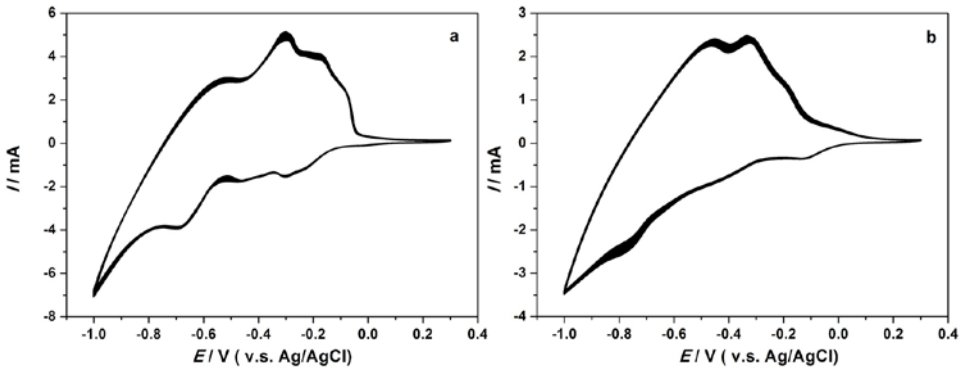

Figure S2 The 100 cycles of CV test of the P_5W_{30}/TiO_2 (a) and S_5W_{30}/TiO_2 (b) film in $LiClO_4$ aqueous solution. (pH=3 adjusted by HCl)

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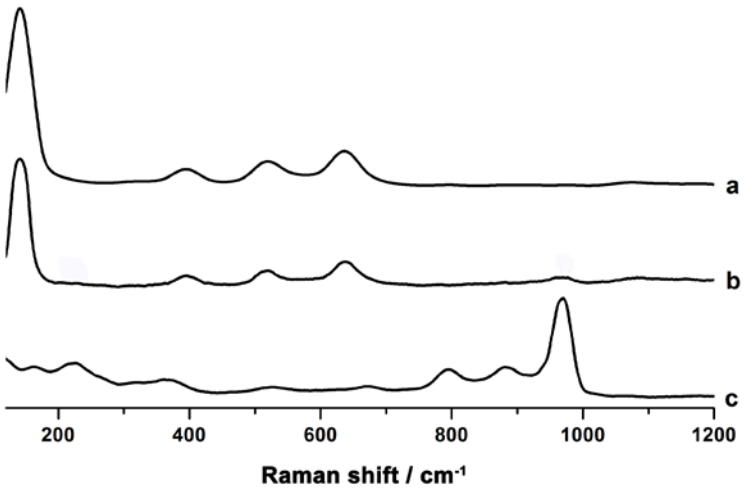

Figure S3 Raman scattering spectra of bare TiO_2 substrate (a), P_5W_{30}-based electrode (b) and pure P_5W_{30} (c)

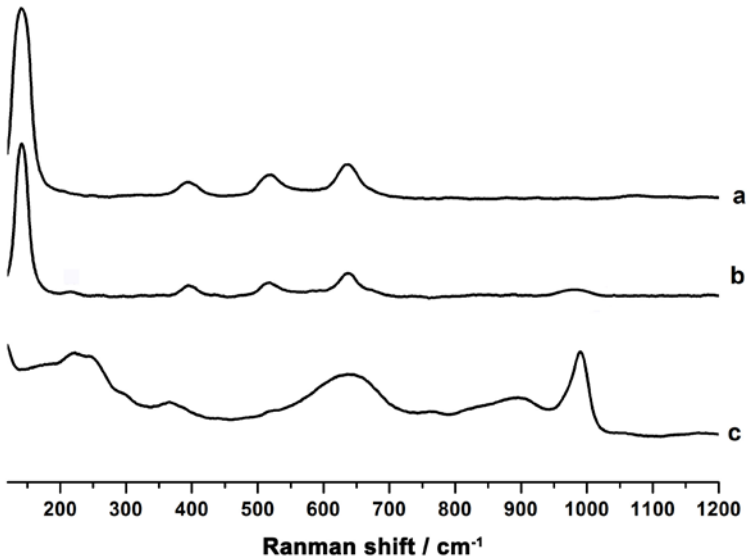

Figure S4 Raman scattering spectra of bare TiO_2 substrate (a), S_5W_{30}-based electrode (b) and pure S_5W_{30} (c)

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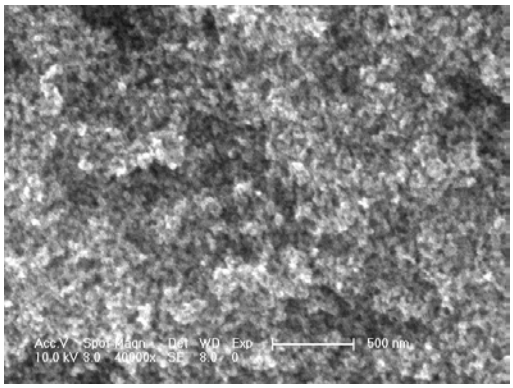

Figure S5 the SEM image of the surface of the as-prepared TiO_2 film.

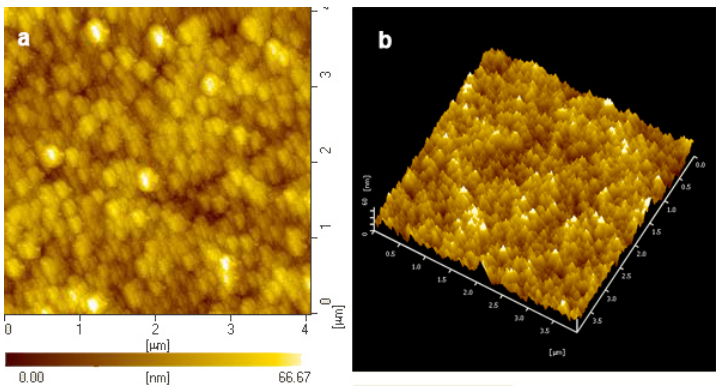

Figure S6 the AFM image of the as-prepared TiO_2 film (a) and the the 3D AFM images of the as-prepared TiO_2 film (b).

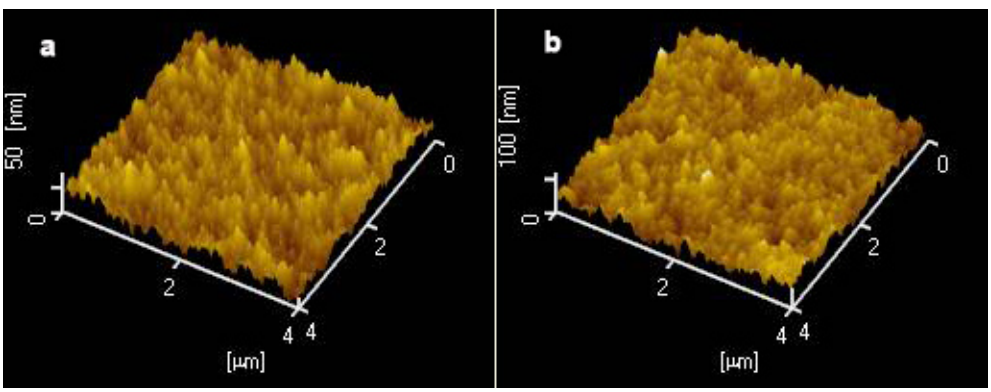

Figure S7 the 3D AFM images of the P_5W_{30} (a) and S_5W_{30} (b) based EC electrodes.

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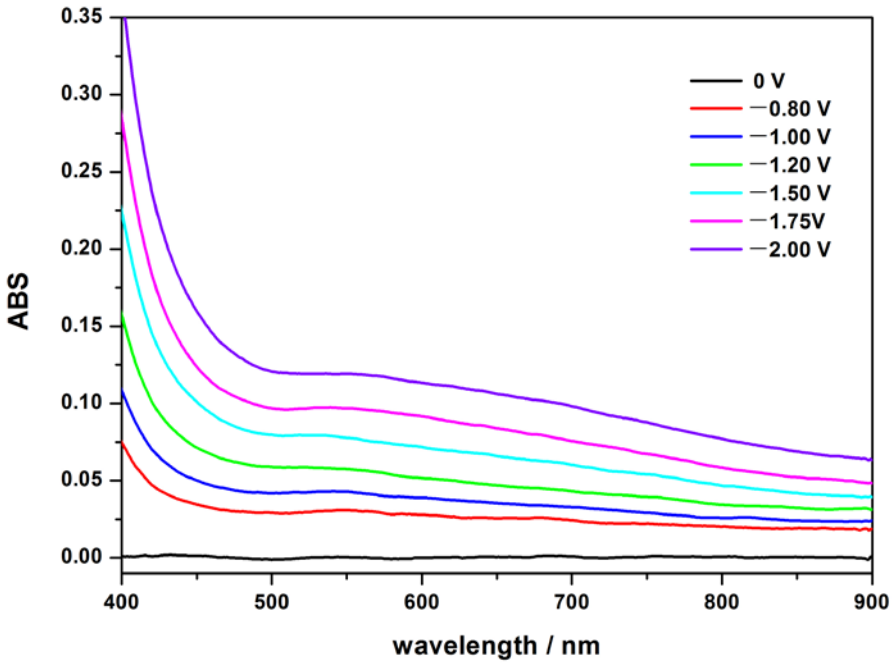

Figure S8 Visible spectra of the smart window based on S_5W_{30} under different potentials ranging from -0.8 to -2.0V.

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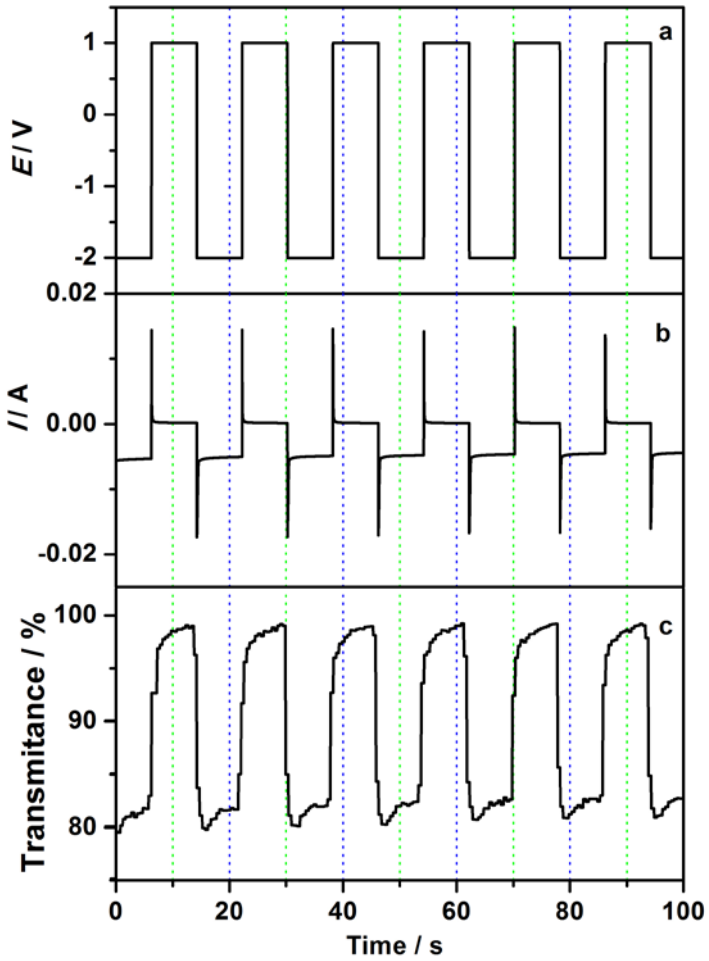

Figure S9 Potential (a), current (b) and absorbance (c) at 550 nm of the smart window based on S_5W_{30} during the subsequent double-potential steps between 1.0 and -2.0V.

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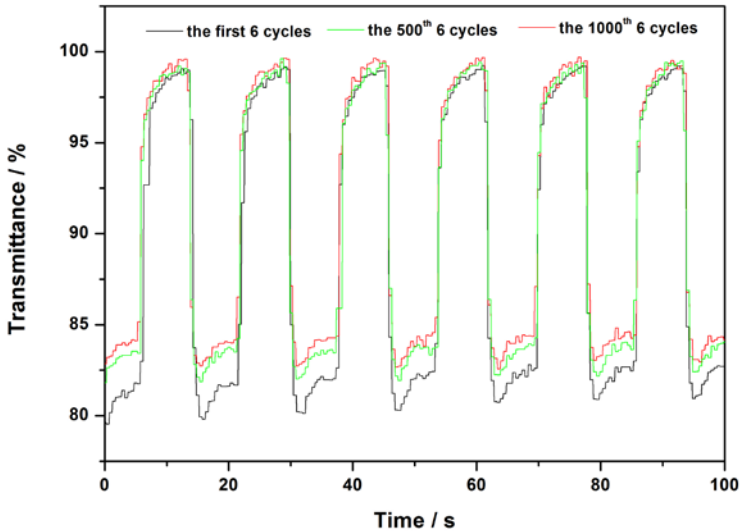

Figure S10 The stability and reversibility of the S_5W_{30}-based smart windows. The black line represents the first 6 cycles of the double-potential steps; the green line represents the 500th 6 cycles of the double-potential steps; the red line represents the 1000th 6 cycles of the double-potential steps.