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MDPI

Supporting Information

An Electrochromic Ag-Decorated WO_{3-x} Film with Adjustable Defect States for Electrochemical Surface-Enhanced Raman Spectroscopy

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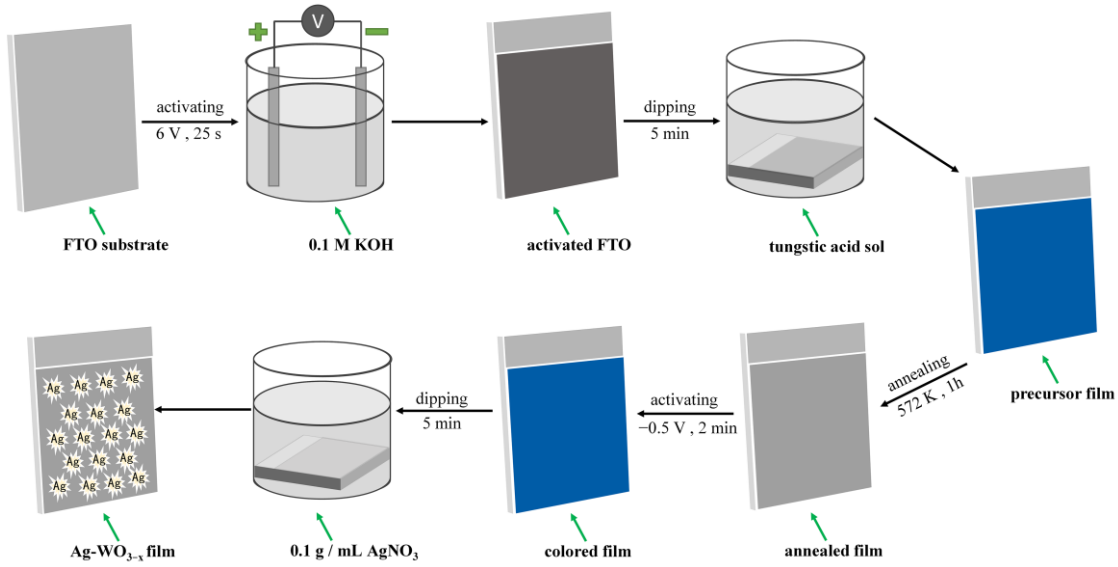

Figure S1. Schematic representation of the synthesis of Ag-WO_{3-x} film through a two-step electrochemical activation.

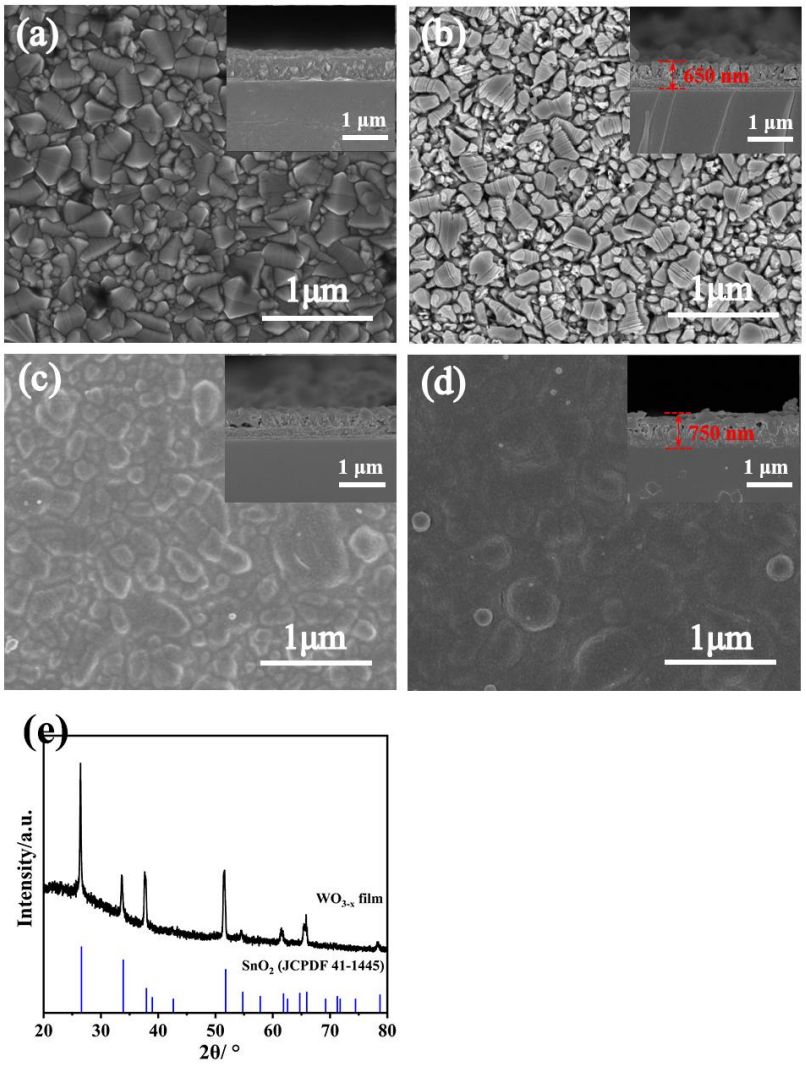

Figure S2. SEM images of (**a**) FTO, (**b**) activated FTO, and WO_{3-x} film (**c**) before and (**d**) after annealing in air at 300 °C for 1 h. (**e**) X-ray diffraction (XRD) pattern of the synthesized WO_{3-x} film. It can be seen that the FTO substrate has many diamond-shaped protrusions with a rough surface, and the protrusions become smooth after electrochemical activation (**a**,**b**). A blue amorphous tungsten trioxide hydrate film was formed on the activated FTO substrate due to the reaction of Sn layer with the polytungstic acid (**c**). After annealing, there is no other obvious change except some tiny cracks on the film surface (**d**). The thickness of the WO_{3-x} film is estimated to be about 100 nm.

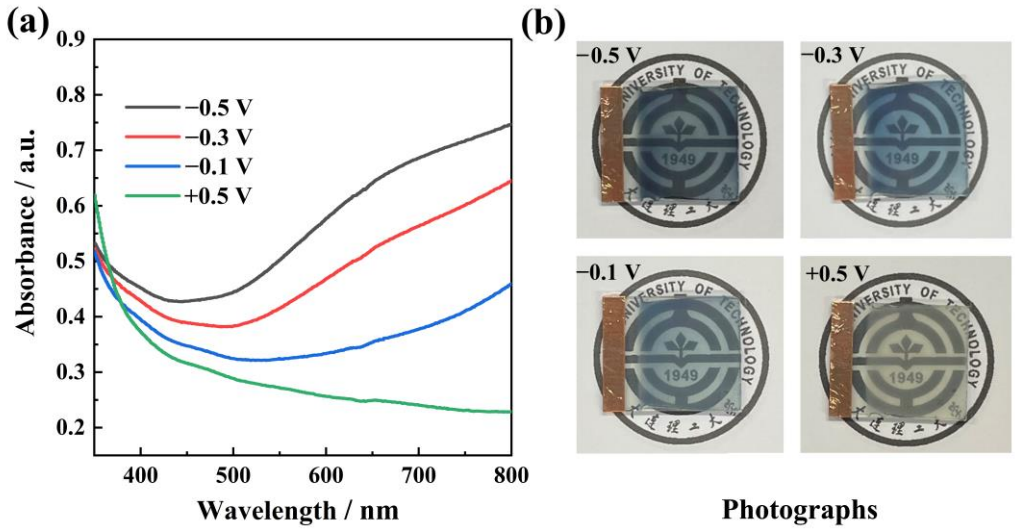

Figure S3. (**a**) UV-Vis-NIR absorption spectra and (**b**) the corresponding photographs of the WO_{3-x} film under the applied potentials of −0.5V, −0.3V, −0.1V and 0.5 V. It can be seen that the degree of discoloration of WO_{3-x} film is deepened by the increase of negative potential, and the WO_{3-x} film returns to a colorless state when a positive potential is applied to the WO_{3-x} film. These results demonstrated the WO_{3-x} film has good electrochemical stability, and the content of reduced tungsten can be flexibly tuned by the applied potential.

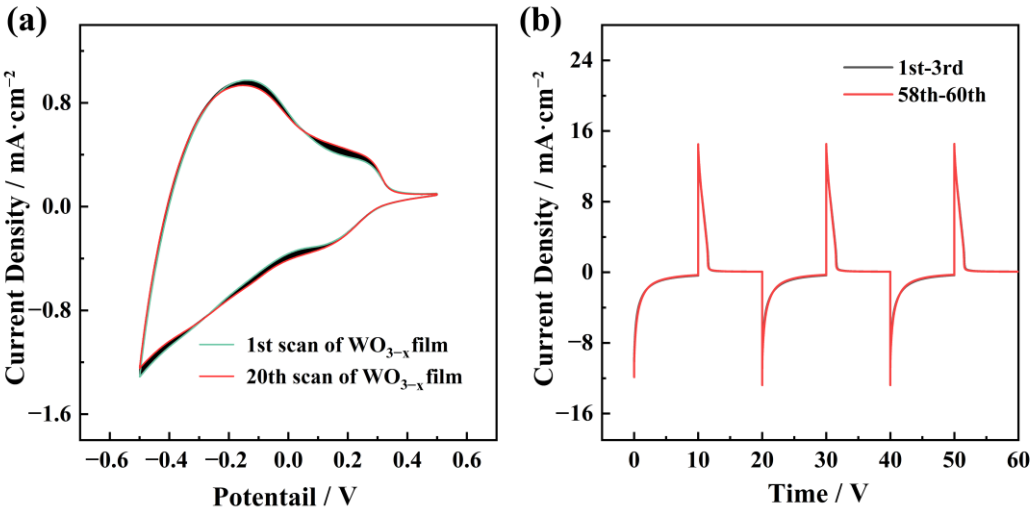

Figure S4. (**a**) CV curves of WO_{3-x} film in 0.1 M H_2SO_4 with a scan rate of 50 $mV \cdot s^{-1}$ for the 20 cycles. (**b**) Chronoamperometry curves of WO_{3-x} film by alternately applying a potential of ±0.5 V, 10 s for each state. The current density of the WO_{3-x} film only slightly decreases after 20 CV cycles, indicating that the WO_{3-x} film has good cyclic stabilities. (**b**) compares the chronoamperometry curves of the WO_{3-x} film for the first three cycles and the last three cycles. There is no obvious change in the current response peak shape, which further confirmed that the WO_{3-x} film shows a good electrochemical stability.

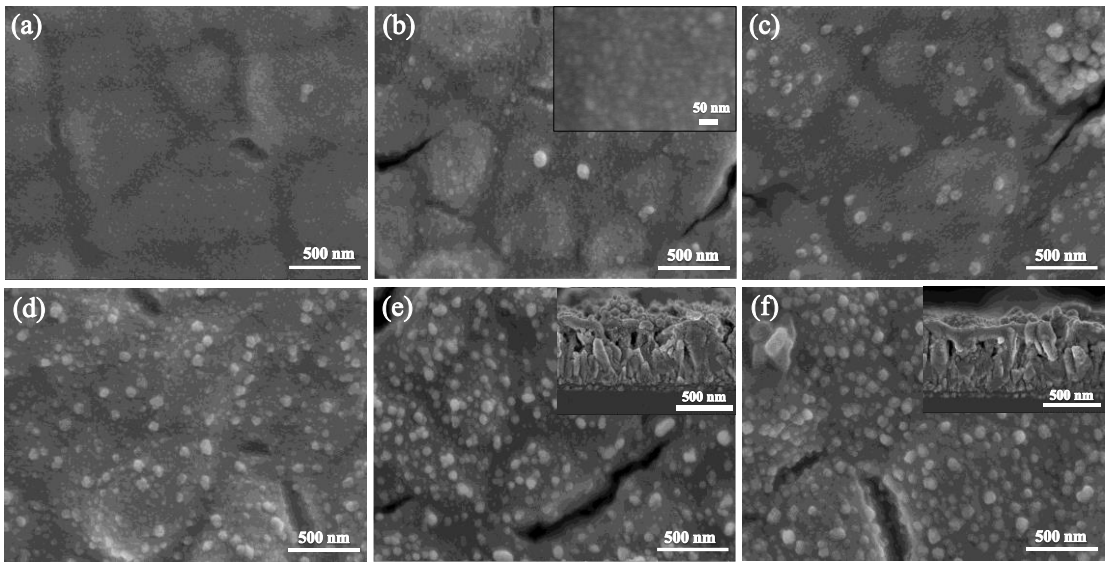

Figure S5. SEM images of the Ag-decorated WO_{3-x} film synthesized by applying of different activated potentials of (**a**) −0.1, (**b**) −0.2, (**c**) −0.3, (**d**) −0.4, (**e**) −0.5, and (**f**) −0.6 V.

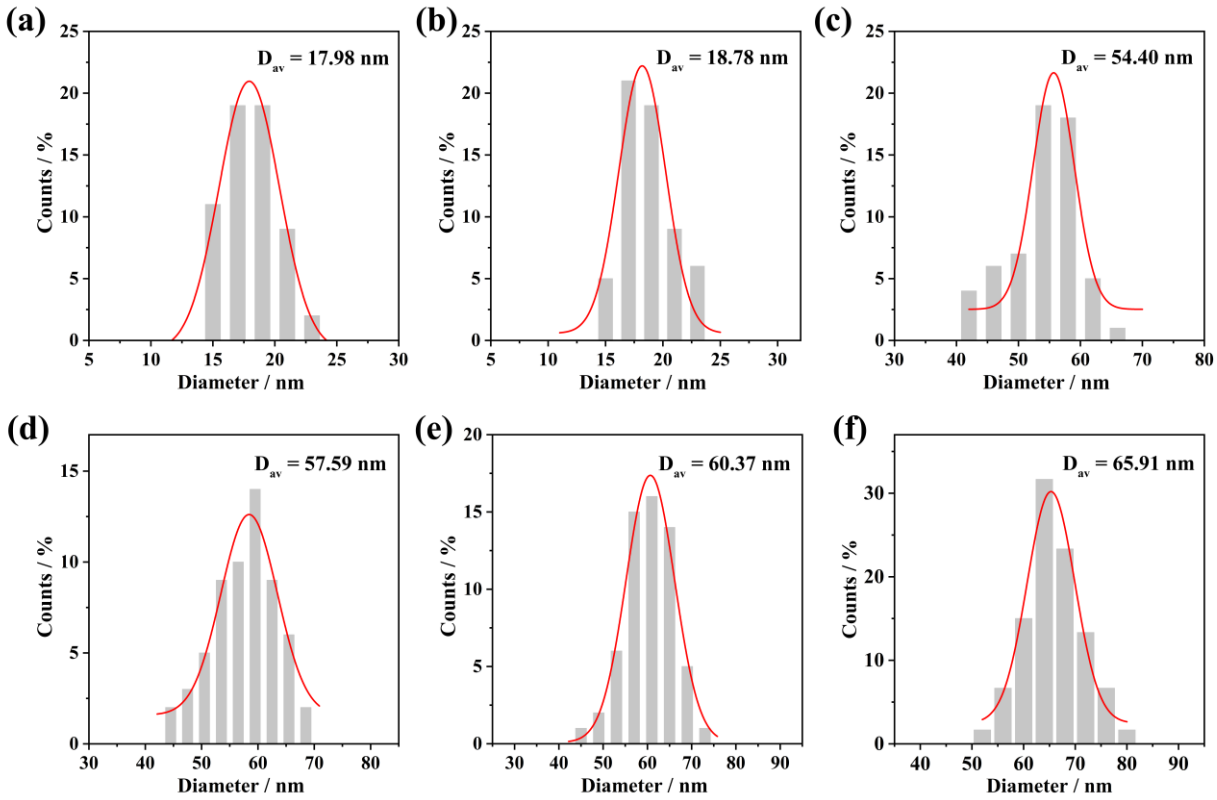

Figure S6. Size distributions of the Ag NPs on the synthesized Ag-WO_{3-x} film under the activation potential of (**a**) −0.1, (**b**) −0.2, (**c**) −0.3, (**d**) −0.4, (**e**) −0.5, and (**f**) −0.6 V.

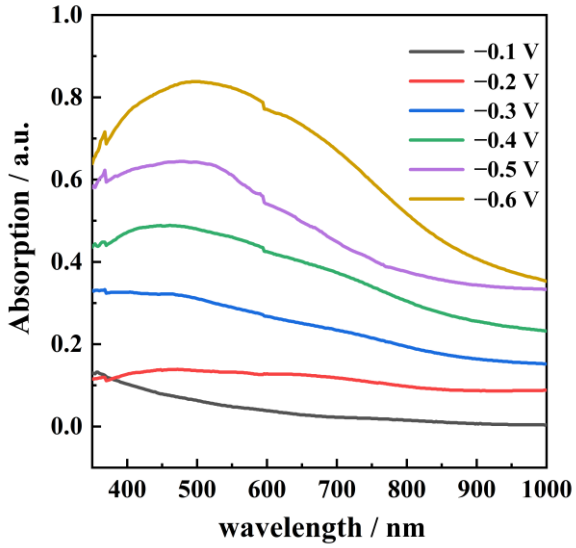

Figure S7. UV-Vis-NIR absorption difference spectra of Ag-decorated WO_{3-x} film synthesized under different applied potentials.

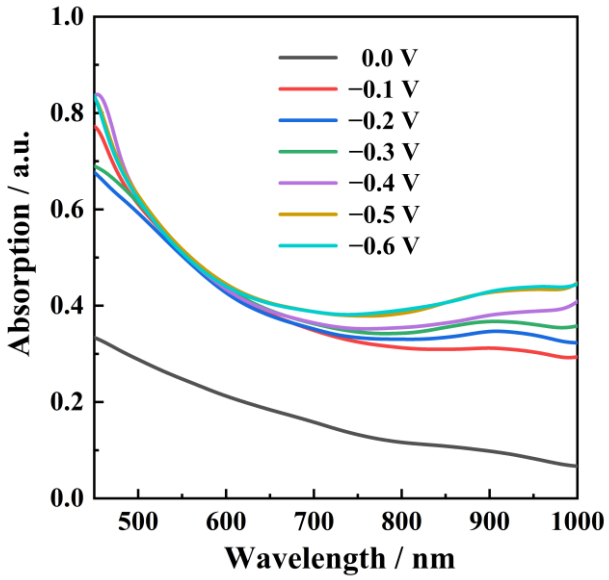

Figure S8. The UV-Vis-NIR absorption spectra of Ag-decorated WO_{3-x} film under different applied potentials.

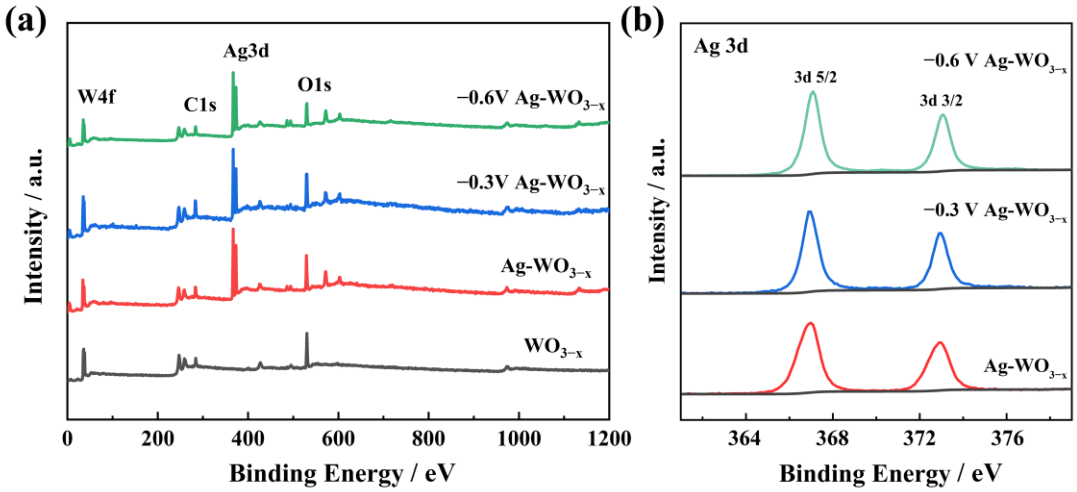

Figure S9. (**a**) Full XPS spectra and (**b**) high-resolution XPS spectra of Ag3d for various of WO_{3-x} and Ag-WO_{3-x} samples.

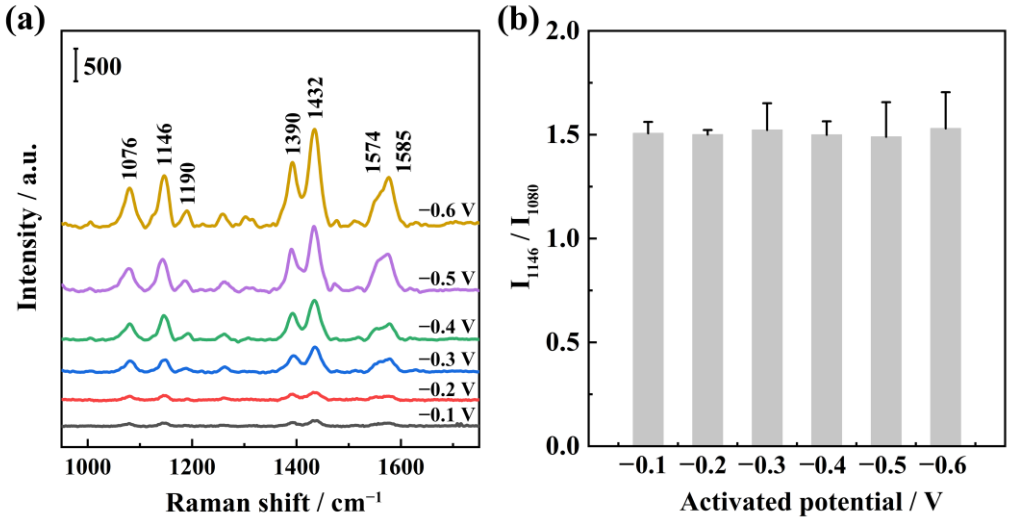

Figure S10. (**a**) SERS spectra of PATP adsorbed on Ag-decorated WO_{3-x} film synthesized under different activated potential. (**b**) Relative intensity of I_{1146}/I_{1080} as a function of the activated potential.

Table S1. The relationship between the activation potential and the diameter of synthesized Ag-WO_{3-x} film.

Activation Potential / V	−0.1	−0.2	−0.3	−0.4	−0.5	−0.6
Diameter of Ag NPs / nm	17.98	18.78	54.40	57.59	60.37	65.91

Table S2. Fitting parameters (peak position, peak area and species percentage) for both W4f 7/2 and W4f 5/2 spectra of XPS taken from WO_{3-x} and Ag-WO_{3-x} activated with different applied potentials.

Sample	Species	B.E. (eV)		Area		W^{5+}/W^{6+}
		4f 7/2	4f 5/2	4f 7/2	4f 5/2	
WO_{3-x}	W^{5+}	35.77	37.94	17110.43	12832.82	0.61
	W^{6+}	35.94	38.11	27981.36	20986.02	
Ag-WO_{3-x}	W^{5+}	-	-	-	-	-
	W^{6+}	34.3	36.47	34332.16	25749.12	
−0.3 V Ag-WO_{3-x}	W^{5+}	34.85	37.02	18363.08	13772.31	3.18
	W^{6+}	34.96	37.12	5781.302	4335.977	
−0.6 V Ag-WO_{3-x}	W^{5+}	34.9	37.07	64308.90	48231.67	11.30
	W^{6+}	35.3	37.47	5692.382	4269.287	