Improving photoelectrochemical properties of anodic WO_3 layers by optimizing electrosynthesis conditions

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1. EDS spectra

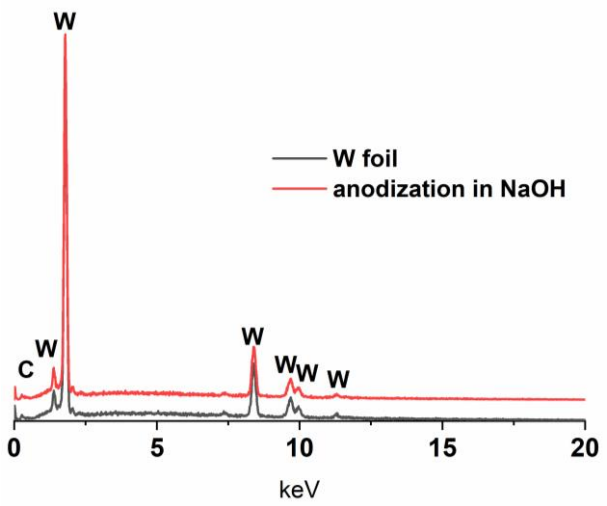

Fig. S1. EDS spectra of tungsten foil and tungsten sample anodized in a 1.8 M NaOH solution.

2. Mott-Schottky analysis

Table. S1. Flat band potentials estimated for all studied WO_3 samples at 200, 500 and 1000 Hz.

WO_3 sample label	Flat band potential / V vs. SCE		
	200 Hz	500 Hz	1000 Hz
B	-0.05	-0.03	-0.08
C	-0.10	-0.15	-0.25
D	-0.15	-0.20	-0.25
G	-0.12	-0.17	-0.20
F	-0.10	-0.18	-0.24

3. UV-Vis reflectance measurements

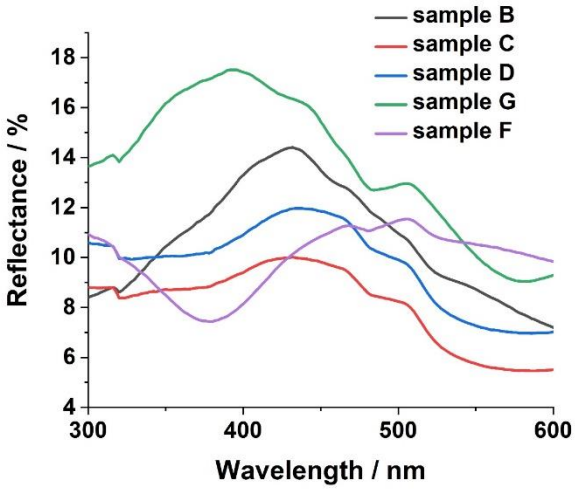

Fig. S2. UV-Vis reflectance spectra for all studied WO_3 samples after anodization and annealing in air at 500 ^oC for 2 h.

The optical band gaps of anodic WO_3 layers were also estimated from UV-Vis diffusion reflectance measurements using the Tauc method (see Fig. 8B). The method is based on the assumption that the absorption coefficient α depends on energy according to the following relation (1):

$$(\alpha \cdot h\nu)^{1/\gamma} = B \cdot (h\nu - E_g) \qquad (1)$$

where h – the Planck constant, ν – frequency of photon, B – constant depending on the material disorder, E_g – the band gap energy, γ – constant depending on the nature of electron transition, which is equal to ½ for direct and 2 for indirect transition band gaps [3, 54]]. The recorded reflectance spectra were transformed to absorption spectra using the Kubelka-Munk function given by the equation (2):

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (2)$$

where: R_∞– reflectance, $F(R_\infty)$ – Kubelka-Munk function [54 – 56]. Since $F(R_\infty)$ is proportional to α, in the next step α in equation 3 can be substituted with $F(R_\infty)$ [54 – 56].

4. Photoelectrochemical response stability

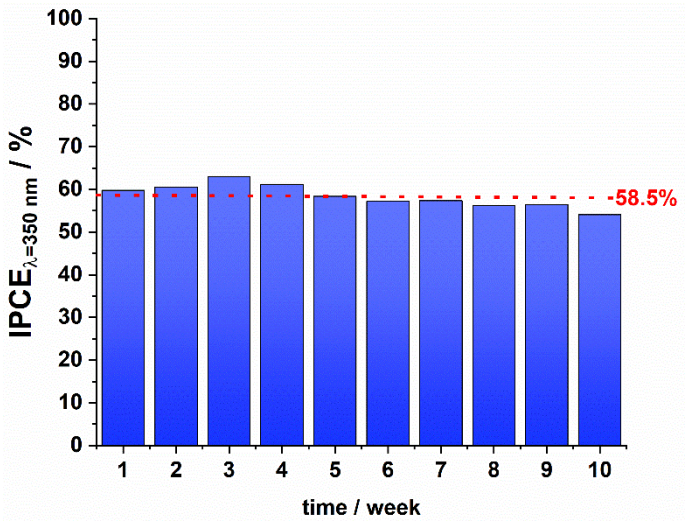

Fig. S3. IPCE values obtained at 1 V vs. SCE for the sample B over 10 weeks of storage with corresponding average response.