Electronic Supporting Information

Experimental details

Photoelectrochemical measurements

Photoelectrochemical experiments were carried out in a one-compartment Teflon cell equipped with a quartz window allowing illumination of the WO_3 film with minimum optical losses. A platinum counter electrode was used and the potential of the WO_3 photoanode was monitored against saturated calomel $Hg/Hg_2Cl_2/Cl^-$ reference electrode and was subsequently converted to be expressed *vs* reversible hydrogen electrode (RHE) in the same solution.
Simulated AM 1.5 solar irradiation was provided by an Oriel 150W solar simulator fitted with a Schott 113 filter and a neutral density filter. In one experiment (*cf.* Fig. 2b),the near-UV illumination was provided by 334.0, 351.1 and 363.8 nm emission lines of argon ion laser.

Structural measurements

The SEM investigations were performed with a Carl Zeiss AURIGA—CrossBeam Workstation. The microscope was equipped with “in lens” and Everhart-Thornley SE detectors, ExB detector and with a bright-field STEM detector.
Raman spectra were collected in the backscattering configuration with a Labram HR800 (Horiba Jobin–Yvon) confocal microscope system equipped with a Peltier-cooled CCD detector (1024 x 256 pixel), using a diode pumped, frequency doubled Nd:YAG laser (532 nm).

Impedance experiments

Impedance measurements were carried out with a Solartron 1286 potentiostat coupled with Solartron 1260 Frequency Response Analyzer controlled by IBM PC compatible computer with the CorrWare 3.0 and ZPlot 3.0a software. The impedance spectra were recorded in the frequency range f = 5 mHz to 10 kHz. The reversible hydrogen electrode was used as a reference electrode. The platinum sheet (*A* ~ 5 cm2) served as a counter electrode.

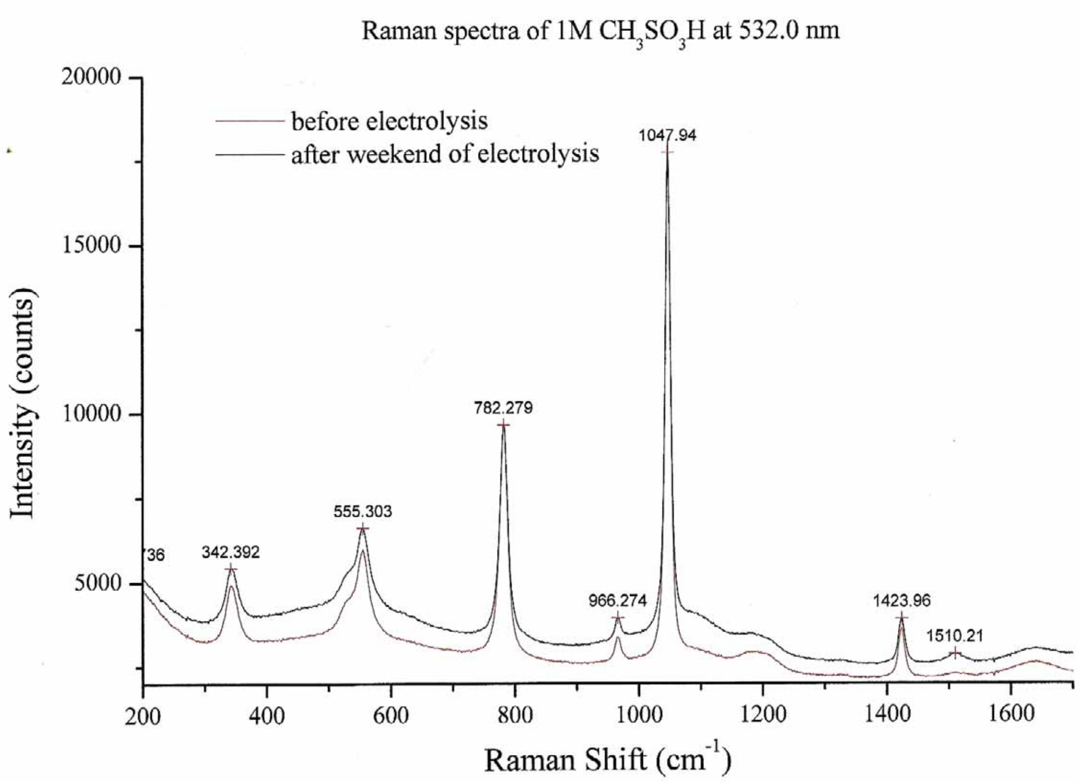
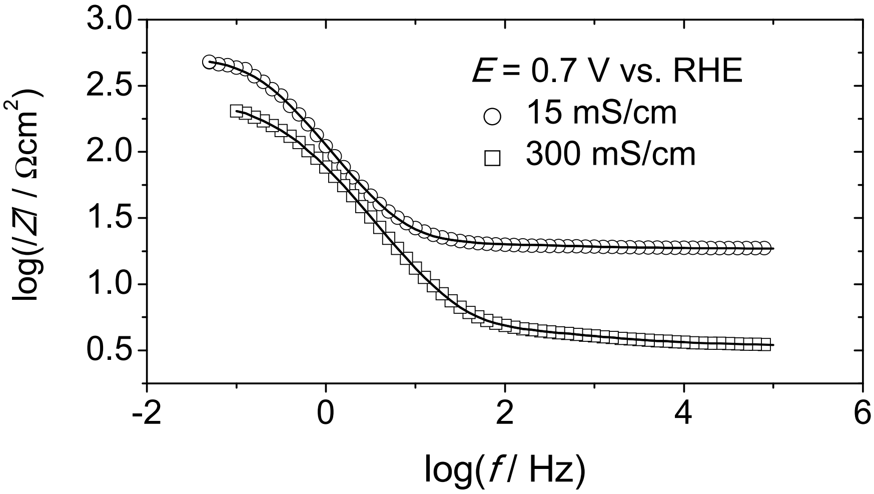


Fig. S1. Raman spectra of a 1 M 1 M CH_3HSO_3 electrolyte before and after 65 h long photoelectrolysis under simulated AM 1.5 irradiation

(a)



(b)

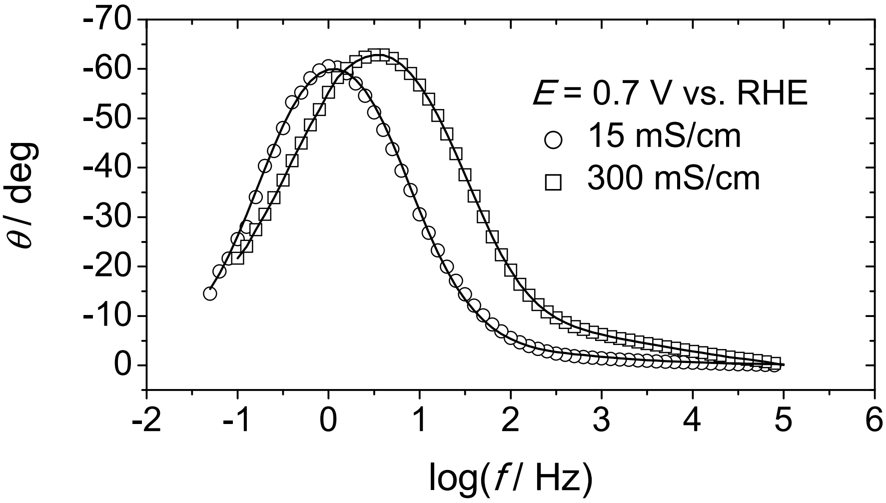


Fig. S2. Bode – modulus (a) and Bode – phase angle (b) plots of impedance measured for 1.4μm thick NS WO_3 film electrode at 0.7 V *vs* RHE in CH_3HSO_3 solutions of two different concentrations: (○) 1 M, 300 $mScm^{-1}$ and (□) 0.04 M, 15 $mScm^{-1}$. Electrode was illuminated with simulated AM 1.5 solar light. Experimental points were fitted to the equivalent circuit shown in Fig. S3.

Bode – modulus and Bode – phase angle plots of impedance are shown in Fig. S2. The graphs of log│Z│ vs. log(*f*) (Fig. S2A) exhibit two breaking points as the curves tend to constant values for extreme frequencies. The high frequency limit of impedance modulus is equal to solution resistance, R_s, while for low frequencies the modulus tends to the polarization resistance determined mostly by the charge transfer resistance, R_{ct}. Bode – phase angle plots are shown in Fig. S2B. The peak position on the frequency scale depends on the system characteristic frequency $f = 1/(R_{ct}C)$, where C denotes the film capacitance. In the case of the results reported herein the latter parameter is only slightly influenced by changes in the specific conductance of the supporting electrolyte. For example, for the spectra shown in Fig. 4a (and S2) the film capacitance changes from $C = 1{,}36$ to 1.17 $mF \cdot cm^{-2}$ for $\sigma = 15$ and 300 $mS \cdot cm^{-1}$, respectively. For the same solutions the charge transfer resistance decreases markedly from $R_{ct} = 484$ to 212 $\Omega \cdot cm^2$, which results in lower time constant for the electrode immersed in the solution of higher specific conductance. Therefore, for a given potential the phase angle peak shifts to higher frequencies with raising specific conductivity of the solution.

Equivalent circuit used for impedance data fitting.

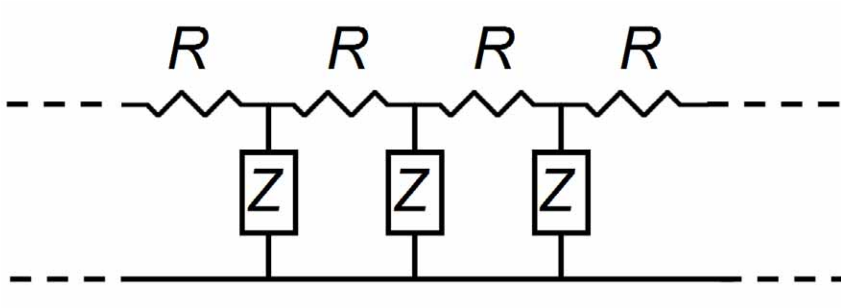


Fig. S3. Uniform transmission line representing impedance of a porous electrode. *R* is the solution resistance and *Z* symbolizes specific impedance of the electrode material – a parallel connection of constant phase element and resistance of the electrode/electrolyte charge transfer $R_{\mathrm{ct,WO3}}$.