Sn-doped Hematite Films as Photoanodes for Photoelectrochemical Alcohol Oxidation

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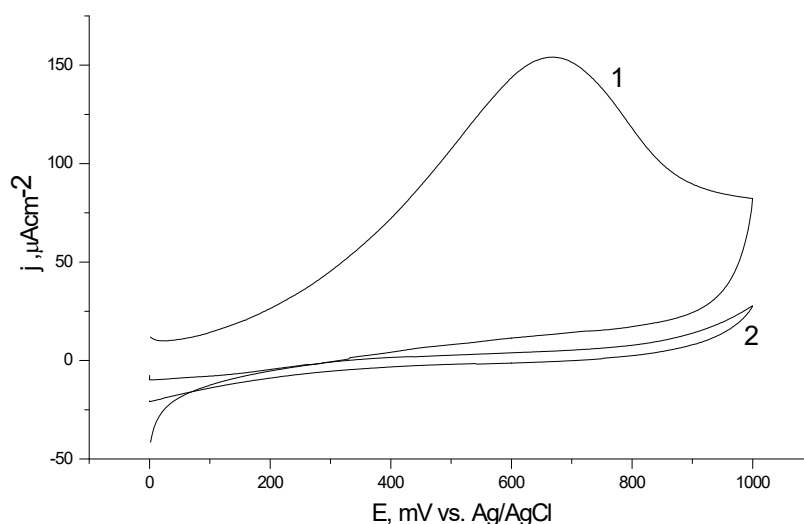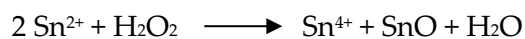
Supplementary materials

Fig. S1. Cyclic voltammogramson glassy carbon electrode ($0.0078 \ cm^{-2}$): (1)–25 mM $SnCl_2$- 0.1 M KCl; (2) – 25 mM $SnCl_2$- 0.1 M KCl + 1M H_2O_2. Scan rate 0.1 Vs^{-1}.

In the presence of H_2O_2 in the electrolyte of film electrodeposition, formation of Sn^{4+} and SnO takes place. Peak of Sn^{2+}oxidation is not observed (CV 2).

$$2 \ Sn^{2+} + H_2O_2 \longrightarrow Sn^{4+} + SnO + H_2O$$

The anodic current peak at 660 mV on cyclic voltammogram (1) can be assigned to the anodic oxidation of the Sn^{2+} to Sn^{4+}. The value of the oxidation current peak indicates that electrooxidation is accompanied by the transfer of two electrons.
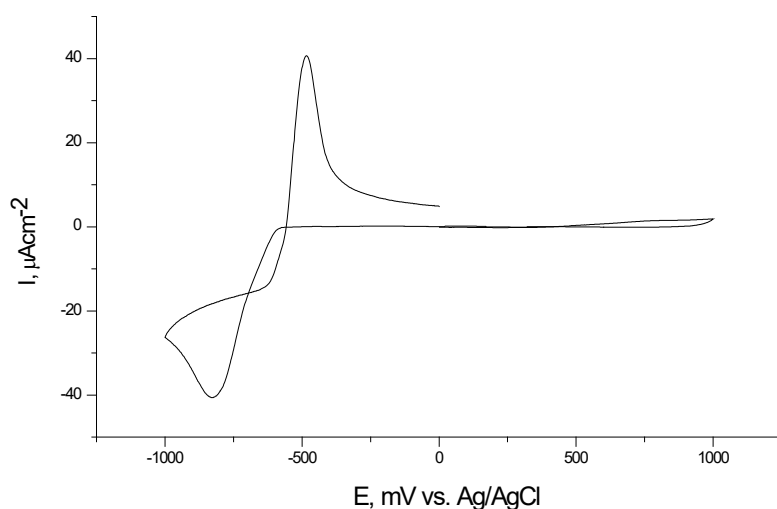
Fig. S2. Cyclic voltammogram of SnCl$_2$ (7.5 mM) on glassy carbon electrode (0.0078 cm^{-2}) in 0.1 M KCl. Scan rate 0.1 Vs^{-1}.
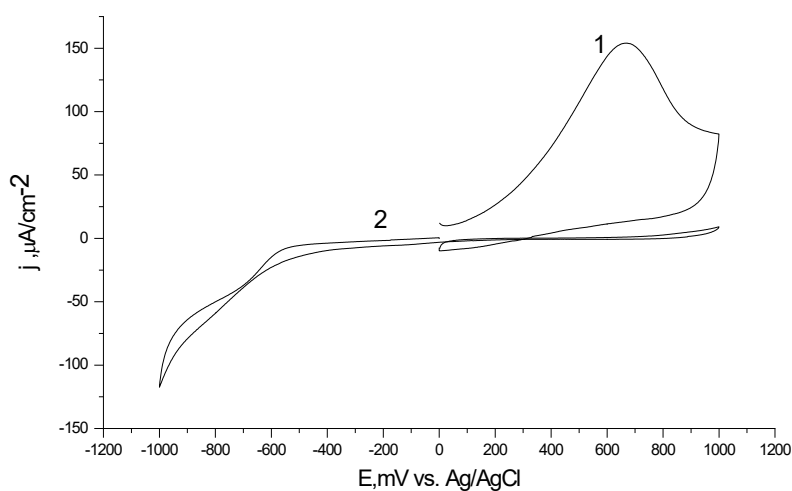

Fig. S3. Cyclic voltammogram of SnCl$_2$ (25 mM) on glassy carbon electrode (0.0078 cm^{-2}) (1) and in the presence of 1M H$_2$O$_2$ (2) in 0.1 M KCl. Scan rate 0.1 V s^{-1}.

The cathodic current density peak is observed at approximately −0.82 V. Thereby, the cathodic current peak could be attributed to the reduction of Sn^{2+} species to metal Sn. A single anodic current peak is observed during the reversal sweep. The anodic current peak isassigned to the anodic stripping of the Sn deposit during the forward scan. The value of potential difference is ~400 mV, which is larger than the theoretical value for the reversible process (31 mV, 323 K). It was typically associated with quasi-reversible electrode reaction process. These characteristics indicate that the reduction of Sn(II) is a quasi-reversible, single-step two-electron-transfer process.
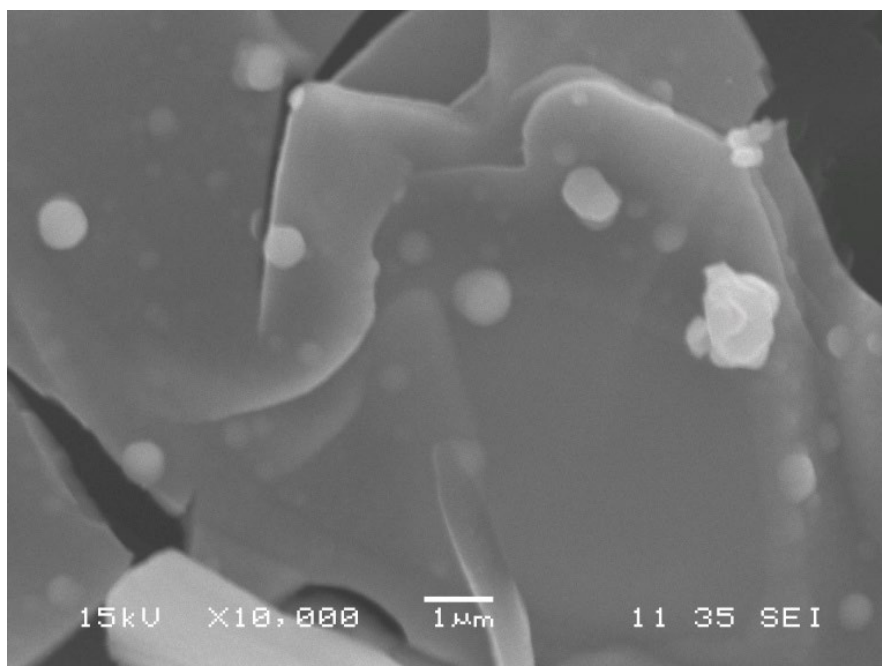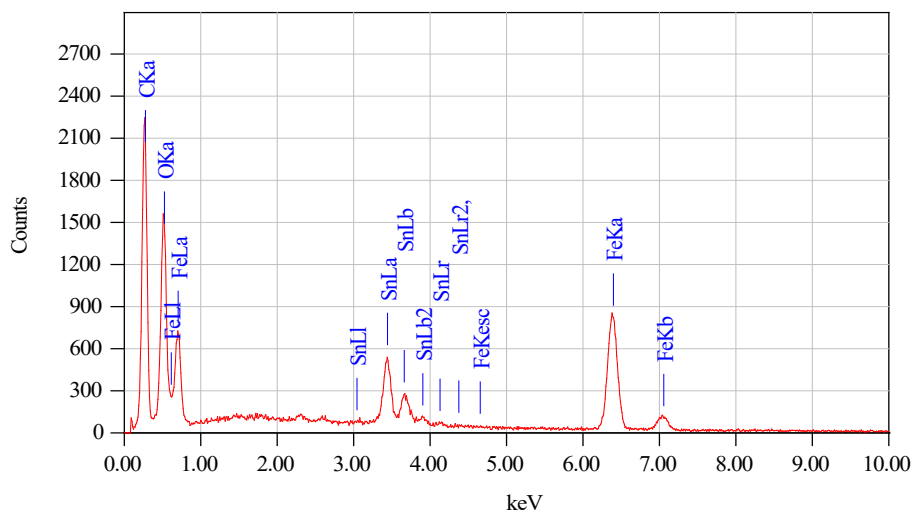
Title   : IMG2

                 Instrument   :

    Volt   : 15.00 kV

    Mag   : x 15,000

    Date   : 2023/10/10

    Pixel   : 640 x 480

Acquisition Parameter

Instrument   : 6060(LA)

Acc. Voltage : 15.0 kV

Probe Current: 1.00000 nA

PHA mode   : T3

Real Time   : 56.64 sec

Live Time   : 50.00 sec

Dead Time   : 11 %
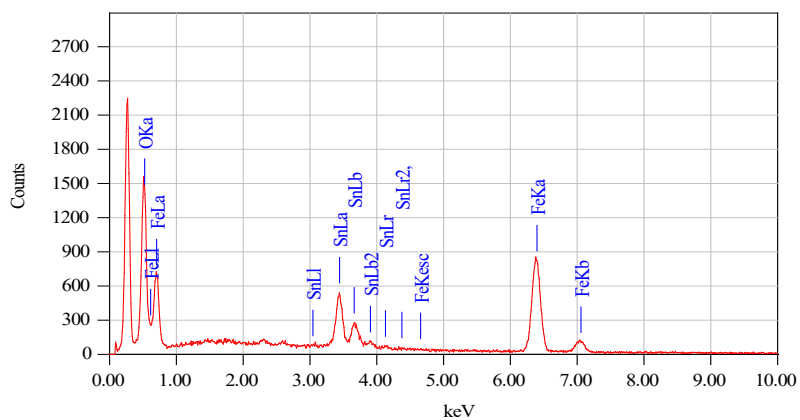
Counting Rate: 2298 cps

Energy Range : 0 - 20 keV

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2075

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K	0.277	30.45	0.02	55.37				17.8793
O K	0.525	20.68	0.08	28.23				20.6259
Fe K	6.398	35.80	0.31	14.00				46.5437
Sn L	3.442	13.06	0.23	2.40				14.9511
Total		100.00		100.00				

Fe:O:Sn= 1: 2.01 : 0.17

Fig. S4a. SEM and EDX spectrum of (α-Fe_2O_3+10% Sn^{4+}) film on a glassy carbon plate

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient: 0.4800

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K	0.525	23.87	0.46	56.11				25.1608
Fe K	6.398	55.44	2.48	37.33				56.6437
Sn L	3.442	20.69	1.89	6.56				18.1955
Total		100.00		100.00				

Fe:O:Sn= 1: 1.5 : 0.17

Fig. S4b. EDX spectrum of (α-Fe_2O_3+10% Sn^{4+}) film excluding carbon of GC substrate
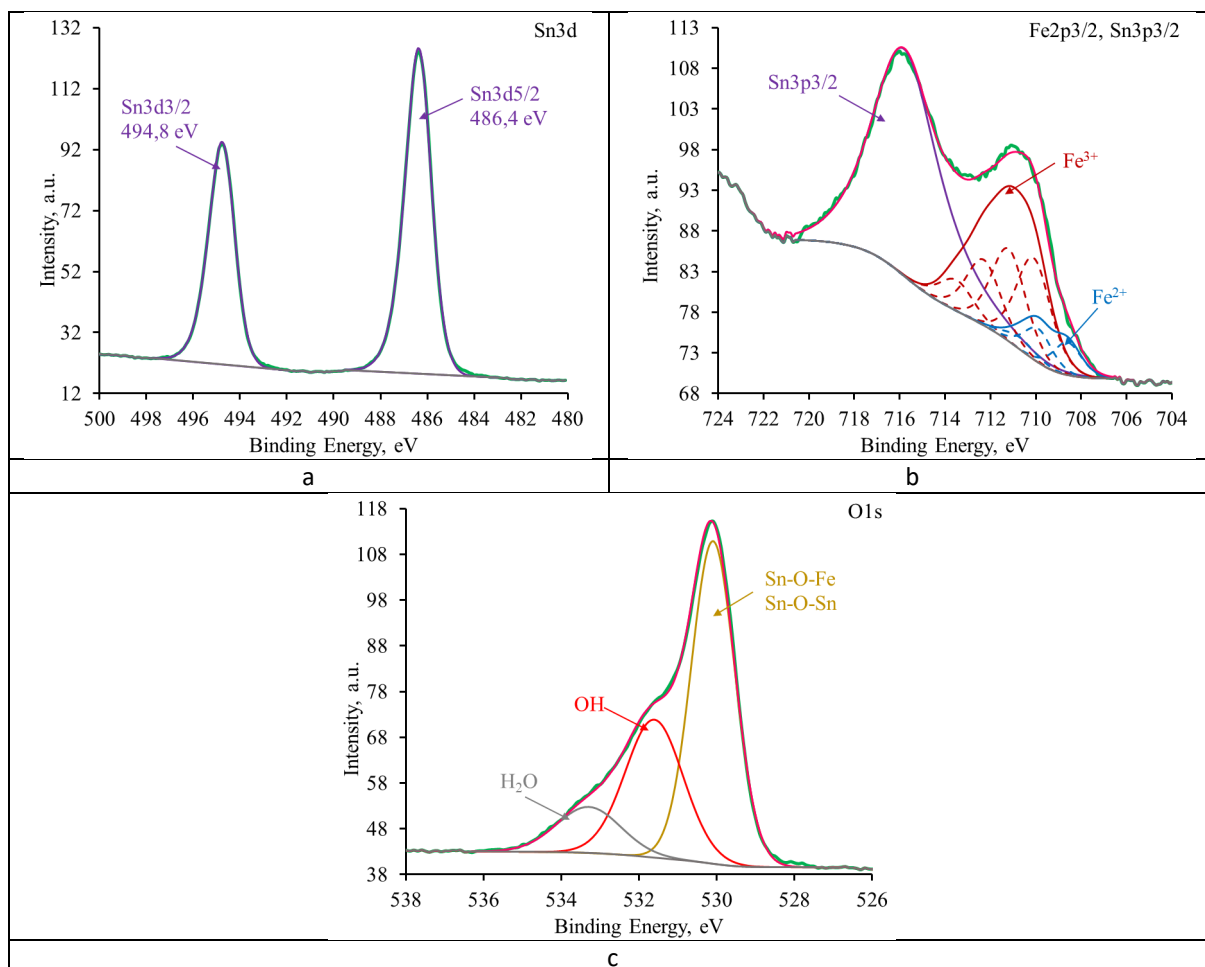
Fig. S5. XPS spectra of (α-Fe₂O₃+10% Sn⁴⁺) film on FTO. Spectrum of tin Sn3d(a), region Fe2p3/2 and Sn3p3/2 (b) and oxygen O1s(c)

Sample surface element concentrations

Peak name		E_b, eV	Quant., at. %	
O1s	Sn-O-Fe	530,1	44,19	69,36
	OH	531,6	25,17	
Sn3d	Sn(IV)	486,4	11,31	11,31
Fe2p3/2	Fe^{3+}	710,5	15,74	19,32
	Fe^{2+}	708,6	3,58	

The chemical state of doped hematite identifed by XPS spectra can be used to understand the chemical valence and bonding situation of element. In this work, spectra in the region of Sn3d (480-500 eV), Fe2p3/2 (704-724 eV) and O1s (526-538 eV) were obtained and analyzed.

According to the obtained curves, in the region of the tin 3d level (Fig.S5a), two peaks of the spin-orbit splitting Sn3d5/2 – Sn3d3/2 are observed with positions of 486.4 and 494.8 eV and a full width at half maximum (FWHM) of 1.37 eV. The intensity ratio [Sn3d5/2]:[Sn3d3/2] is 3:2. Due to the small shift between the Sn3d5/2 maxima for Sn(II) and Sn(IV), it is not possible to unambiguously determine the state from the experimental curve.

To more accurately determine the iron states, the Fe2p3/2 spectrum was used (Fig. S5b). In this spectrum, there is an overlap of peaks related to iron and the tin peak Sn3p3. Sn3p3 peaks at 715.8 eV and FWHM 3.6 eV. The iron states were adjusted according to [63] with an increase in FWHM for the peaks relative to those presented in the above article by a factor of 1.4 due to the difference in transmission energies and

differences between the morphology of the powder and the surface of the coated plate. According to the results, after subtracting the background and isolating the tin component, iron is in two states, which can be attributed to Fe^{3+} with a maximum of 710.5 eV and Fe^{2+} with a maximum of 708.6 eV.

The oxygen O1s spectrum (Fig. S5c) can be fitted with three peaks. The most intense one with a maximum of 530.1 eV and FWHM of 1.4 eV can be attributed to the Sn-O-Fe and Sn-O-Sn bonds. The peak at 531.6 eV (FWHM 1.8 eV) is in the hydroxide region and is designated OH in the figure, and there is also a peak at 533.3 eV, which can be attributed to water vapor adsorbed from the air or remaining after the coating process.

Using the integrated peak intensities, as well as elemental sensitivity coefficients, the atomic concentrations of elements on the surface of the sample were determined, which are presented in Table . Based on the concentrations, we can assume the presence of $Fe(OH)_3$, which is probably an agent that binds deeper layers with the tin of the coating, where each tin atom forms a bond through oxygen with Fe^{3+} cations in most cases and a small number of atoms bonded through Sn-O-Fe^{2+}-O-Sn.
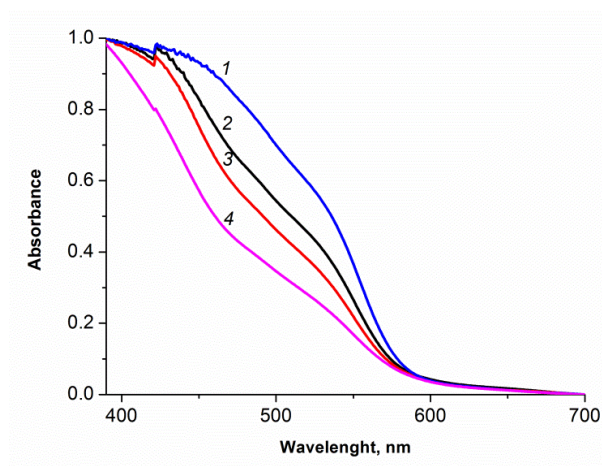

Fig. S6. Normalized absorption spectra for the film photoanodes: (*1*) – (α-Fe_2O_3); (*2*)– (α-Fe_2O_3+ 5% Sn^{4+}); (3) (α-Fe_2O_3+10%Sn^{4+}); and (4) – (α-Fe_2O_3+20%Sn^{4+}).
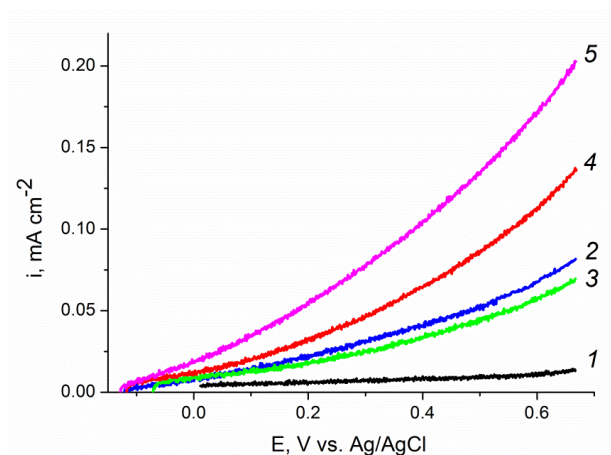

Fig. S7. Voltammograms of the (α-Fe_2O_3) film photoanode: (1) – dark voltammetry in 0.1 M KOH; (2 - 5) – voltammetry curves measured under visible light illumination with a power density of 100 mW cm^{-2} in aqueous solutions. The measurements were performed in electrolytes: (2) – 0.1 M KOH; (3) – 0.1M KOH + 20% CH_3OH; (4) – 0.1 M KOH + 20% $C_2H_4(OH)_2$; (5) – 0.1 M KOH + 20% $C_3H_5(OH)_3$. Potential scan rate is 10 mV s^{-1}. Voltammograms in dark conditions for the alcohol-containing electrolytes solutions practically coincide with (1).
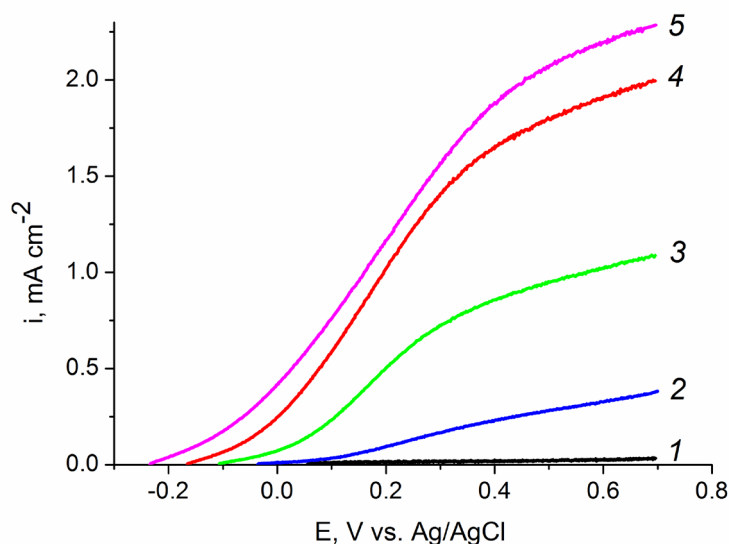
Figure S8. Voltammograms of the (α-Fe$_2$O$_3$+5% Sn^{4+}) film photoanode: (1) – dark voltammetry in 0.1 M KOH; (2 - 5) under visible light illumination with a power density of 100 mW cm^{-2}. The measurements were performed in electrolytes: (2) – 0.1 M KOH; (3) – 0.1M KOH + 20% CH$_3$OH; (4) – 0.1 M KOH + 20% C$_2$H$_4$(OH)$_2$; (5) – 0.1 M KOH + 20% C$_3$H$_5$(OH)$_3$. Potential scan rate is 10 mV s^{-1}. Voltammograms in dark conditions for the alcohol- containing electrolytes solutions practically coincide with (1).
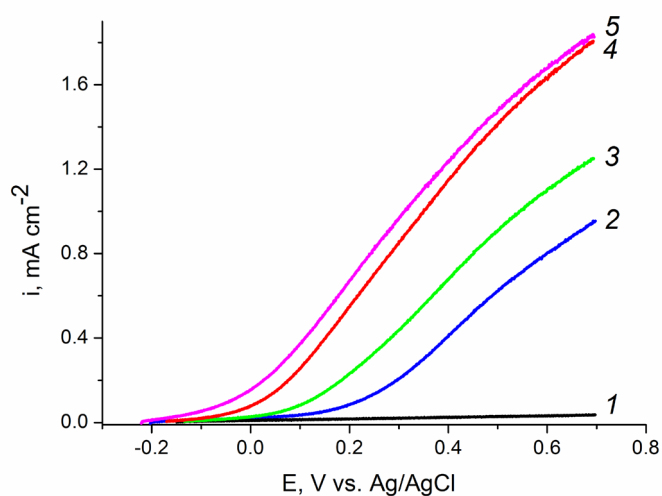

Fig. S9. Voltammograms of the (α-Fe$_2$O$_3$+20% Sn^{4+}) film photoanode: (1) dark voltammetry 0.1 M KOH; (2 - 5) – under visible light illumination with a power density of 100 mW cm^{-2}. The measurements were performed in electrolytes: (2) – 0.1 M KOH; (3) – 0.1M KOH + 20% CH$_3$OH; (4) – 0.1 M KOH + 20% C$_2$H$_4$(OH)$_2$; (5) – 0.1 M KOH + 20% C$_3$H$_5$(OH)$_3$. Potential scan rate is 10 mV s^{-1}. Voltammograms in dark conditions for the alcohol- containing electrolytes solutions practically coincide with (1).
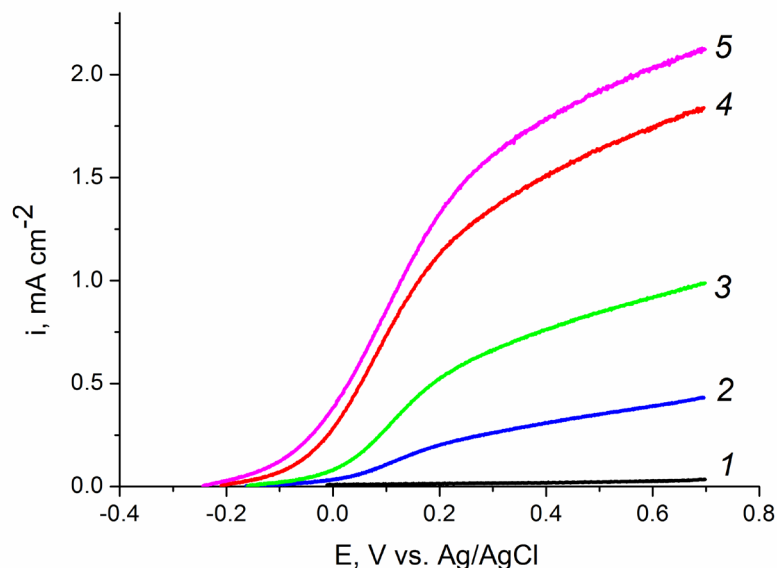
Fig. S10. Voltammograms of the (α-Fe$_2$O$_3$+10% Sn^{4+}) 75 s film photoanode: (1) dark voltammetry 0.1 M KOH; (2 - 5) – under visible light illumination with a power density of 100 mW cm^{-2}. The measurements were performed in electrolytes: (2) – 0.1 M KOH; (3) – 0.1M KOH + 20% CH$_3$OH; (4) – 0.1 M KOH + 20% C$_2$H$_4$(OH)$_2$; (5) – 0.1 M KOH + 20% C$_3$H$_5$(OH)$_3$. Potential scan rate is 10 mV s^{-1}. Voltammograms in dark conditions for the alcohol- containing electrolytes solutions practically coincide with (1).
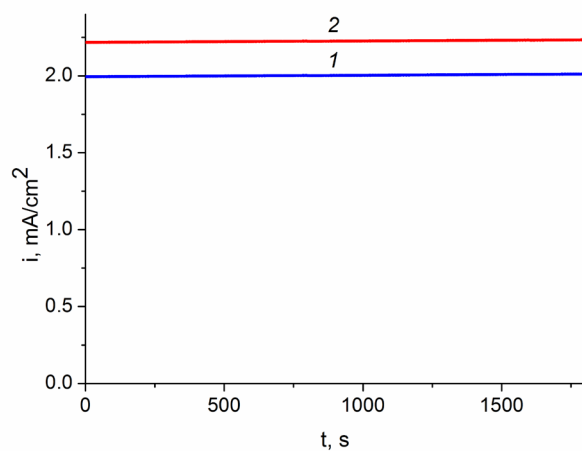

Fig. S11. Photocurrent variation with time measured with(α-Fe$_2$O$_3$+10% Sn^{4+})film photoanode at E =0.4 V– (1) and at E=0.6 V vs. Ag/AgCl – (2) under visible light illumination with a power density of 100 mW cm^{-2} in 0.1 M KOH + 20% C$_3$H$_5$(OH)$_3$.
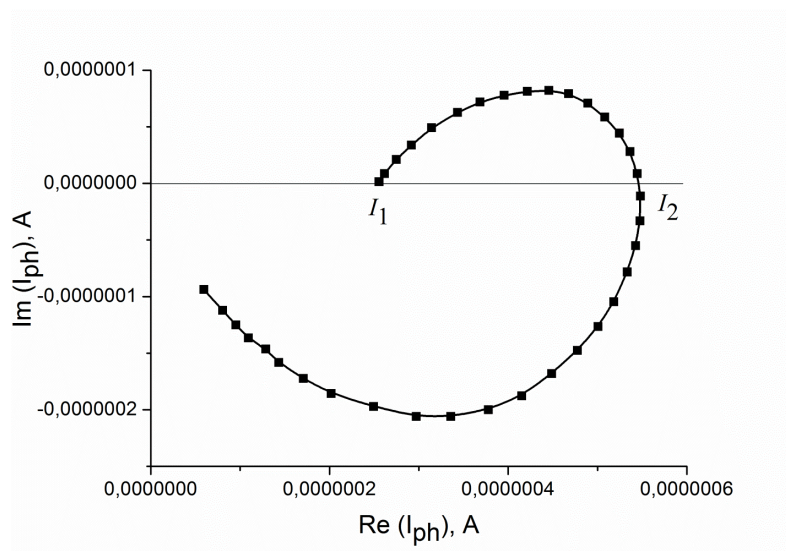
Fig. S12. IMPS curve measured at (α-Fe$_2$O$_3$+10% Sn^{4+}) photoanode illuminated with monochromatic light of 453 nm at the illumination power density of 14 mW cm-2 at E=0.5 V *vs*. Ag/AgCl in 0.1 M KOH.