

SUPPORTING INFORMATION

CoAPO5 as water oxidation catalyst and light sensitizer

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Hydrothermal synthesis of CoAPO5. CoAPO5 was synthesized according to a patented method [1]. In a typical synthesis, N,N-diethylethanolamine (DEA) was used as surfactant, appropriate sources of Al and P for sol-gel processes were added as well as Cobalt acetate in order to obtain the following nominal composition of the synthesis mixture: 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.1 CoO : 1.6 DEA : 80 H₂O. The gel was crystallized in a Teflon-lined stainless-steel autoclave at 473 K for 3 days. The organic surfactant was then removed by calcination in flowing air at 823 K.

Characterization of CoAPO5. The metal content in the samples was determined by an ICP elementary analysis system (OPTIMA 7000 DV ICP/OES Perkin Elmer). Crystallinity of powders was analyzed by X-ray diffraction (Philips Xpert Diffractometer); the obtained spectra are shown in figure S1. UV-VIS spectroscopy of the powdered samples (see figure S2 and following paragraph) was carried out in the diffuse reflectance mode using a Varian model Cary 500 spectrophotometer with a quartz cell suitable for measurements on powders.

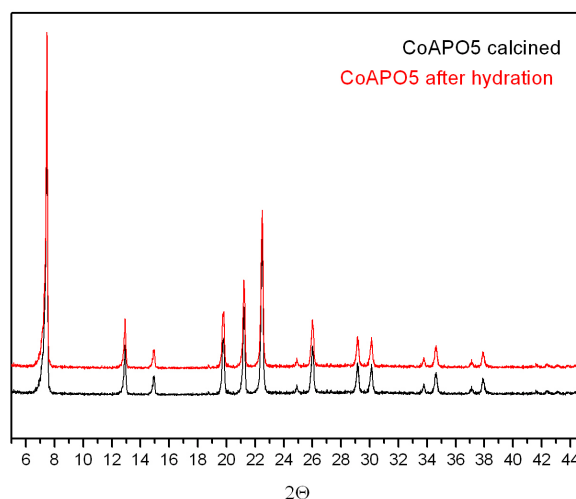


Figure S1. XRD spectra of the obtained CoAPO5 before and after reaction with liquid water.

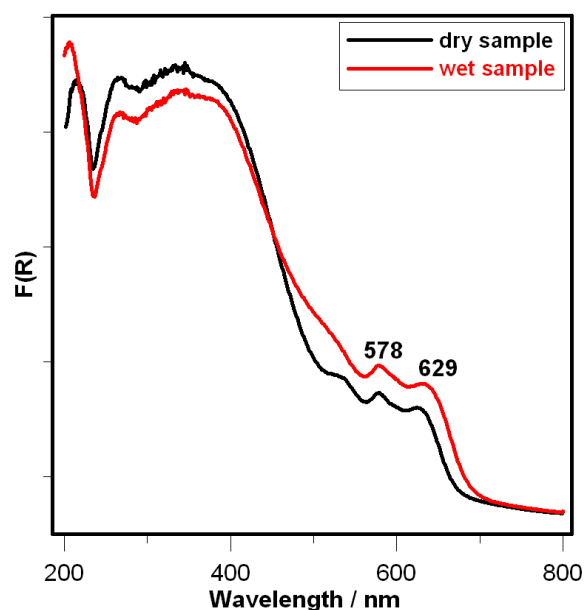
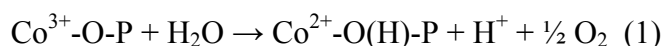


Figure S2. UV-VIS spectra of calcined CoAPO5 (3% w/w Co) before (black line) and after (red line) treatment with liquid water. Two maxima are clearly resolved in the visible region with an energy of 2.15 eV and 1.97 eV respectively.

XRD spectrum. The XRD pattern of the CoAPO5 sample both as-synthesized and after treatment with water is shown in Figure S1. Highly crystalline material with AFI crystal structure was obtained. No extra peaks related to impurities such as transition-metal oxide were observed. The XRD spectrum of the sample after treatment with water does not show any changes in the crystal structure related to hydrolysis or other processes.

UV-VIS analysis of CoAPO5. The spectrum of the calcined sample (Figure S2, black line) shows a triplet band in the region 535-620 nm (20000 -15000 cm^{-1}) ascribable to Co^{2+} in tetrahedral coordination. The broad absorptions in the regions 200-500 nm (40000-20000 cm^{-1}) and 1000-1800 nm (9000-8000 cm^{-1}) are respectively assigned to $\text{O} \rightarrow \text{Co}^{3+}$ [1, 2] and $5\text{T}_2 \rightarrow 5\text{E}$ transitions of tetrahedral Co^{3+} units [2-5]. When the sample is reacted with liquid water (Figure S2 red line), the intensity of the triplet band in the region 535-620 nm (20000 -15000 cm^{-1}) due to Co^{2+} tetrahedral species increases simultaneously with the decrease in intensity of the large bands [200-500 nm (40 000-20 000 cm^{-1}) and 1000-1800 nm (9000-8000 cm^{-1})] related to the Co^{3+} species. Hence, a reduction of Co^{3+} to Co^{2+} species by water is taking place. The pH of the suspension is observed to decrease, so that the reduction of Co^{3+} by water may be expressed as the following reverse charge-transfer reaction:



Electrochemical and Photoelectrochemical setup. Electrochemical and photoelectrochemical measurements were performed into a homemade double compartment glass electrochemical cell (Scheme S1). Electrochemical measurement were performed by a CH instrument 660D electrochemical station in water (from Millipore Mod. SIMS00000) containing 0.1 M K_2SO_4 (from Sigma Aldrich) as supporting electrolyte. The working electrode consisted of a 4 cm^2 FTO (Fluorine Doped Tin Oxide) slide from Solaronix (Resistivity: 30 $\Omega\cdot\text{cm}$) coated with a Nafion[®] (Quintech 5% w/w isopropanol solution) film containing 20 mg of CoAPO5 catalyst. The Counter electrode was a Pt slide and reference was a commercial sat. Ag/AgCl (CH instruments). A Solaronix Mod. INT-30-10 discharge lamp with 28 V power supply was used as simulated solar light source during photoelectrochemical experiments. The lamp was positioned on an optical bench

and light was directed by a metal tube to the cell window in order to obtain an intensity of about 1000 W/m^2 (~ 1 sun) at a suitable distance from cell set by using a Delta Ohm Mod. HD 2102.2 photometer equipped with a LP 471 RAD photodiode (spectral range 400-1050 nm). A manual shutter was used to modulate illumination inside a dark room. A Newport high pass optic density filter (Mod. FSQ-OD110, wavelength $> 400 \text{ nm}$) was used to cut UV light from the source whenever necessary.

FTO/Nafion[®]/CoAPO5 photoanode preparation. 20 mg of calcined CoAPO5 were dispersed in 300 μL of 5% w/w Nafion[®] isopropanol solution (From Quintech) and sonicated for 15 minutes. Successively, the solution was dropped on a sticky tape delimited FTO slide (2x2 cm square) and left to dry for 12 h. Another procedure giving a film with the same electrochemical and photoelectrochemical properties is the following: 20 mg of CoAPO5 are dispersed in 300 μL of isopropanol and dropped onto the FTO slide and left to dry for 12 h; successively 300 μL of 5% w/w Nafion[®] isopropanol solution was dropped and left to dry for 12 h. By varying the relative position of light source and CoAPO5 active layer, three different illumination geometries are possible that are summarized in Scheme S2.

Estimation of Photons to “Holes” conversion uantum yield. To calculate the number of photons hitting the photoanode in the unit of time the following energy distribution histogram, specific of our lamp, has been taken into account.

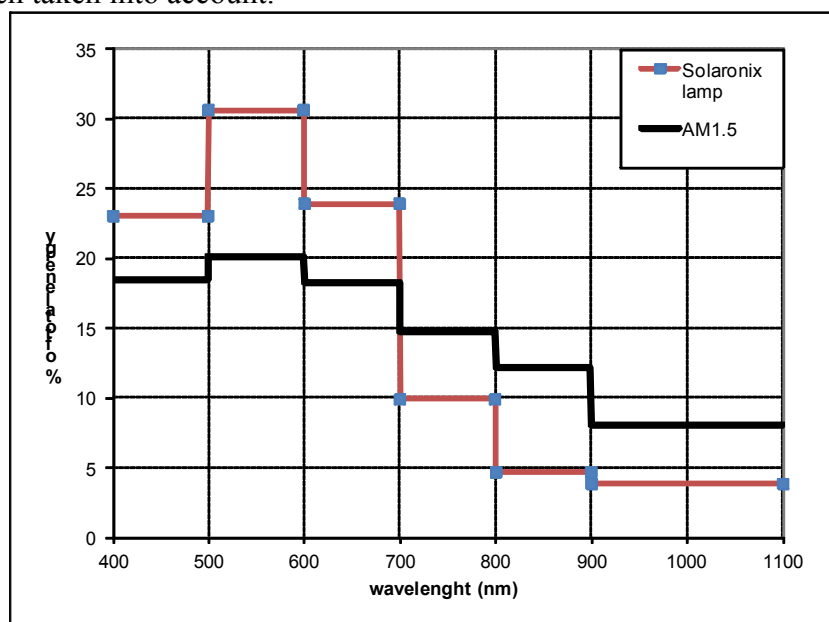


Figure S3. Histogram showing the approximate distribution of the electromagnetic Energy in function of wavelength in 100 nm intervals for solar light (black line) and the plasma lamp employed during our experiments (red line). Data was provided by Solaronix.

In the case of CoAPO5 with UV filtered plasma lamp the spectral range of light absorption is limited to the 400-650 nm range. Considering that the lamp power is of 1000 W/m^2 we obtain that in 400-500 nm interval the total power is 230 W/m^2 and the average Energy of Photon (450 nm) is $4.41 \times 10^{-19} \text{ J}$ by obtaining that the total number of photons/ m^2s is 5.2×10^{20} . In the same way we obtain 8.3×10^{20} photons / s m^2 in 500-600 nm spectral range and 3.8×10^{20} photons / s m^2 in 600-650 nm spectral range. The total is then of 1.73×10^{21} photons / s m^2 . Thus, we have 6.9×10^{17} hitting photons /s in the area of the photoanode (4 cm^2).

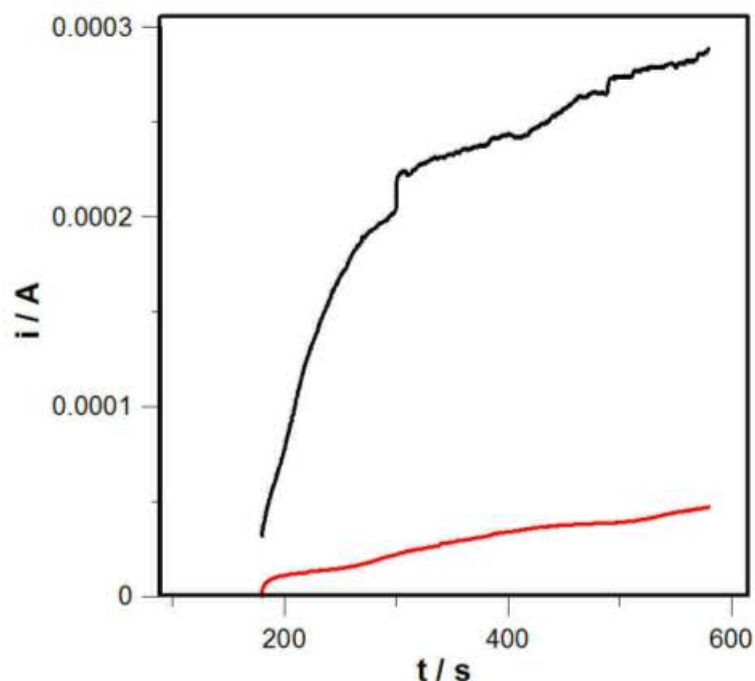


Figure S4. Current Increase vs. time during illumination for Nafion/FTO (Red Line) and FTO/Nafion/CoAPO5 Photoanode (Black line). Light intensity: 1000 W/m²; E = +1.6 V vs. Ag/AgCl; Photoanode area.: 4 cm²; quantity of CoAPO5: 20 mg for FTO slide.

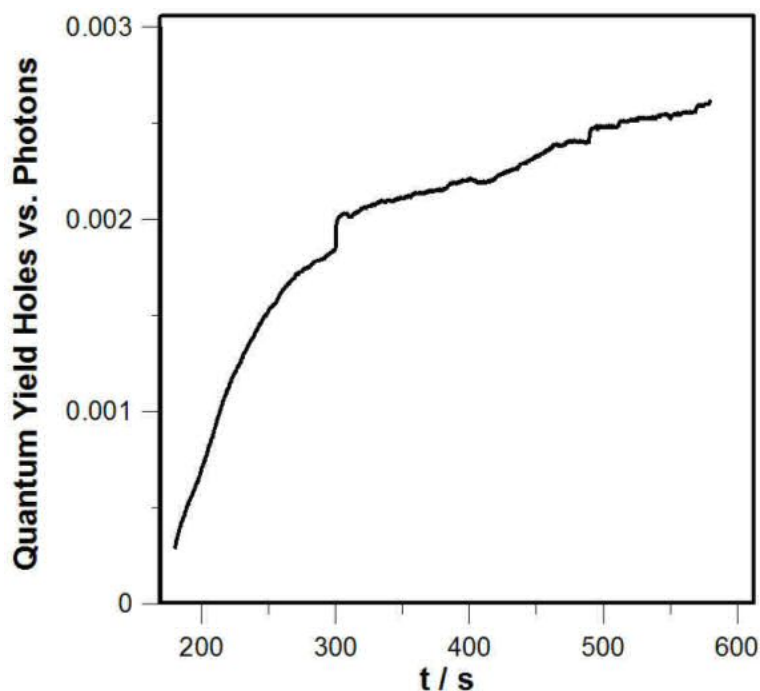


Figure S5. Time Plot of Quantum Yield of electron “holes” produced per photon for illuminated FTO/Nafion/CoAPO5 Photoanode. Experimental conditions are the same described in Figure S4.

In Figure S4 we show the difference of current, expressed in A, between illuminated and non-illuminated Nafion/FTO Photoanode and CoAPO5/Nafion/FTO Photoanode (Same data of Figure 2). Let's assume for simplicity that all current increase is due to photo-induced water oxidation. To obtain the number of electronic “holes” generated by light we simply divide the current by the charge of electron ($1,602 \cdot 10^{-19}$ C). After that we can calculate the instantaneous quantum yield of “holes” generation with respect to photons by dividing the photocurrent curve expressed in electrons number by the number of incident photons on the same surface that is constant vs. time.

The resulting curve (Figure S5) shows that “holes” generation yield after a period of ca. 2 minutes stabilizes in the range of 0.2- 0.25 %.

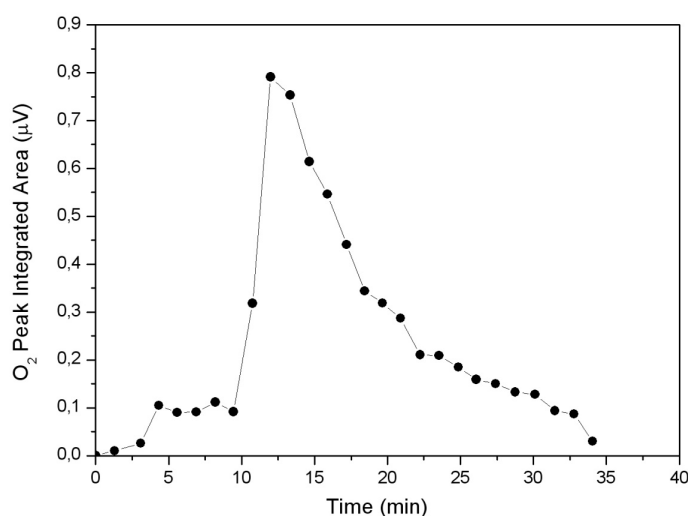


Figure S6. Integrated area of oxygen peak. Argon flowed through cell headspace during electrochemical measurements (ca. first 10 min.) and then through solution until it was no longer detected any gas.

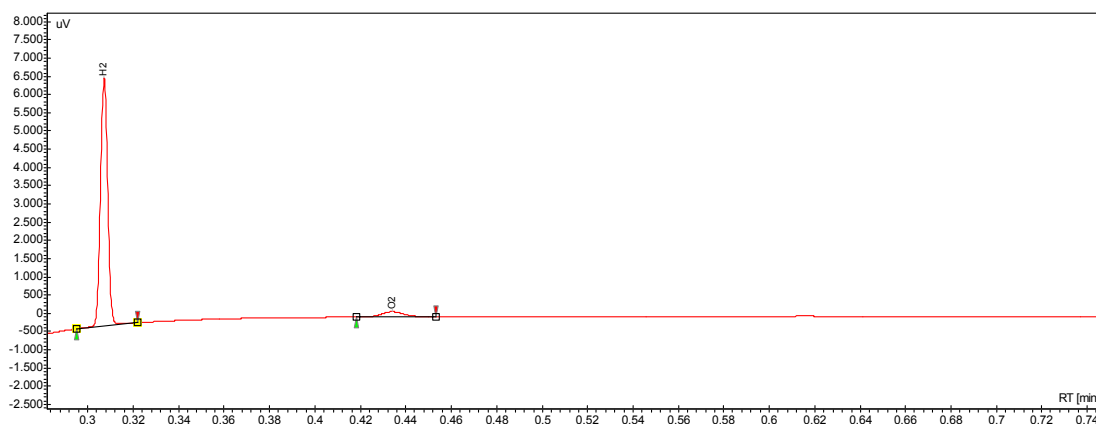
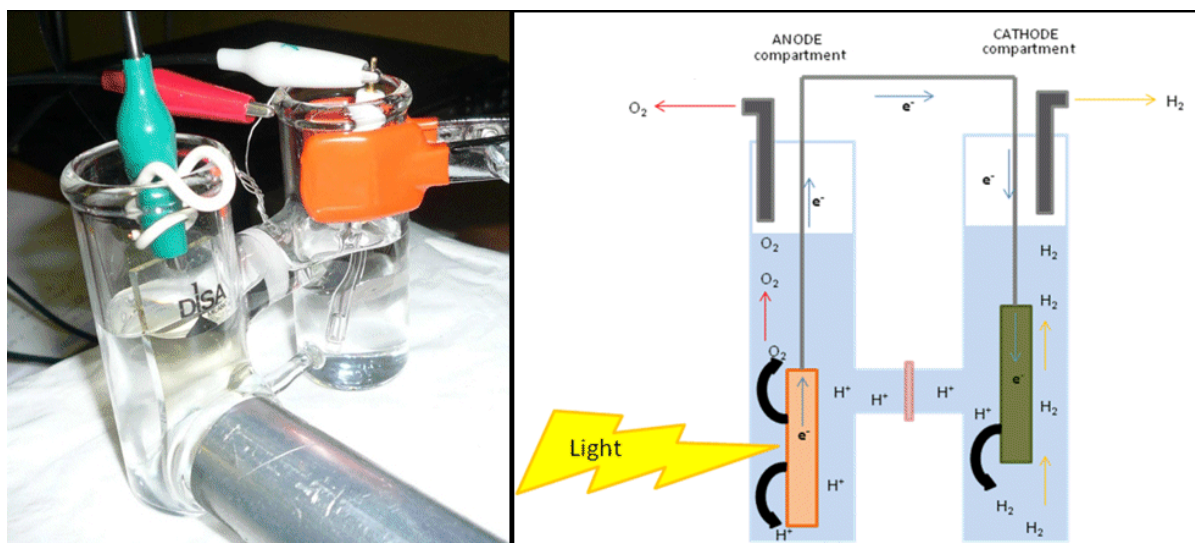
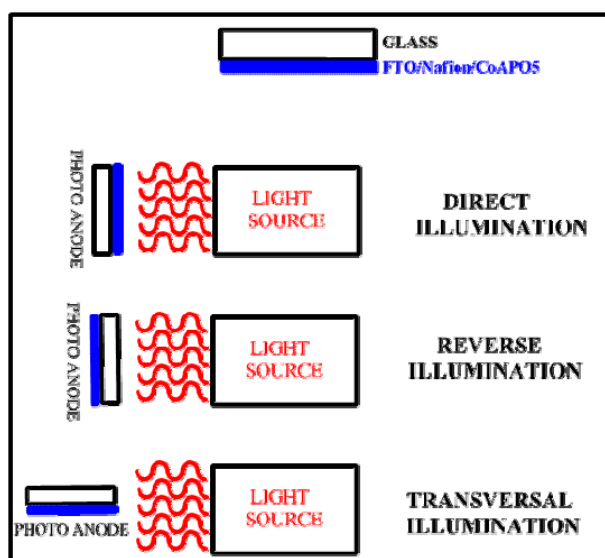


Figure S7. A typical chromatogram registered during illumination of FTO/Nafion/CoAPO5 Photoanode biased at +1.6 V vs. Ag/AgCl. Only two peaks are presents i. e. those related to O₂ and H₂ production.

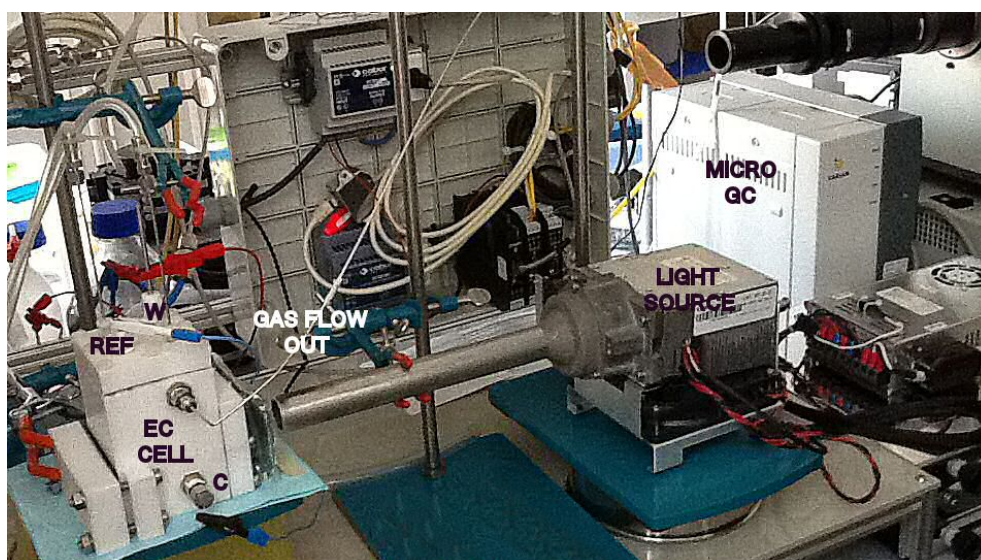
Oxygen and Hydrogen evolution measurements by gascromatography(GC) . Oxygen evolution at FTO/Nafion/CoAPO5 photoanode were followed by performing Current vs. Time measurements in a sealed Teflon cell operating under Ar flow (20 NmL/min) and directly coupled with a Micro-GC (Varian 490-microGC equipped with a Molsieve 5A column (10m) and a micro-TCD detector, Scheme S3). A three-way valve allowed switching the gas feed from the cell headspace to the solution (i.e. bubbling through the solution). During a preliminary purge stage, Ar was bubbled through electrolyte solution, ensuring the complete oxygen removal from both the solution and the cell headspace. Thus, during electrochemical measurements (first 10 min in Fig S6), the Ar flow was switched to the cell headspace and magnetic stirring was stopped (as bubbling and stirring were found to significantly increase signal noise). In these conditions most of the formed oxygen remains dissolved in solution. Only at the end of the current measurement, Ar flow was re-conveyed through the solution and magnetic stirring was re-started in order to strip and detect all dissolved oxygen. During the whole experiment only hydrogen and oxygen peak were present in recorded chromatograms (Figure S7).



Scheme S1. Scheme of the experimental setup for photoelectrochemical measurements.



Scheme S2. Relative position of light source and photoanode during photocurrent measurements.



Scheme S3. View of the setup for combined electrochemical and gaschromatographic measurements. Electrochemical cell for measurement of oxygen / hydrogen evolution was developed in collaboration with HYSYTECH s.r.l.

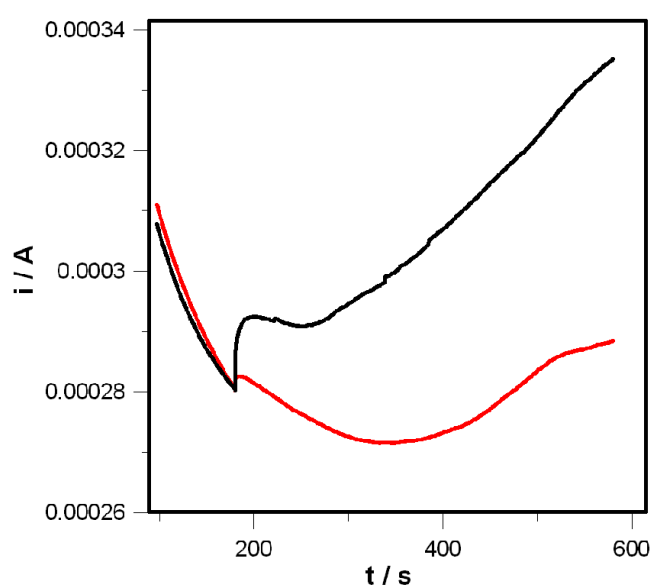


Figure S8. Current vs. Time curve for transversal slide illumination (red curve) and frontal illumination (black line). Photoanode was FTO/Nafion[®] (blank) in 0.1 M K₂SO₄ solution. Light program: 0-180 s dark; 180-580 s light intensity of 1000 W/m². A constant potential of +1.6 vs. Ag/AgCl was applied.

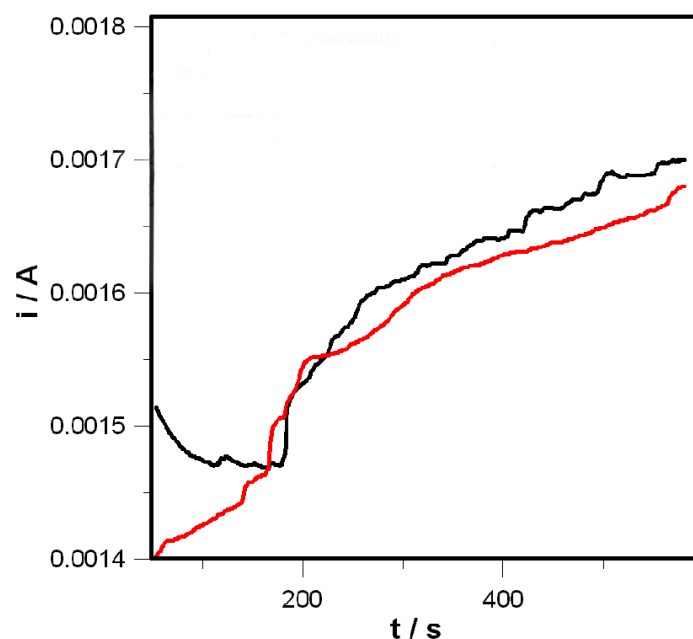


Figure S9. Current vs. Time curve for UV filtered (wavelength > 400 nm, red curve) and full spectrum illumination (black line). Photoanode is FTO/Nafion/CoAPO5 in 0.1 M K₂SO₄ solution. Light program: 0-180 s dark; 180-580 s light intensity of 1000 W/m². A constant potential of +1.6 vs. Ag/AgCl is applied.

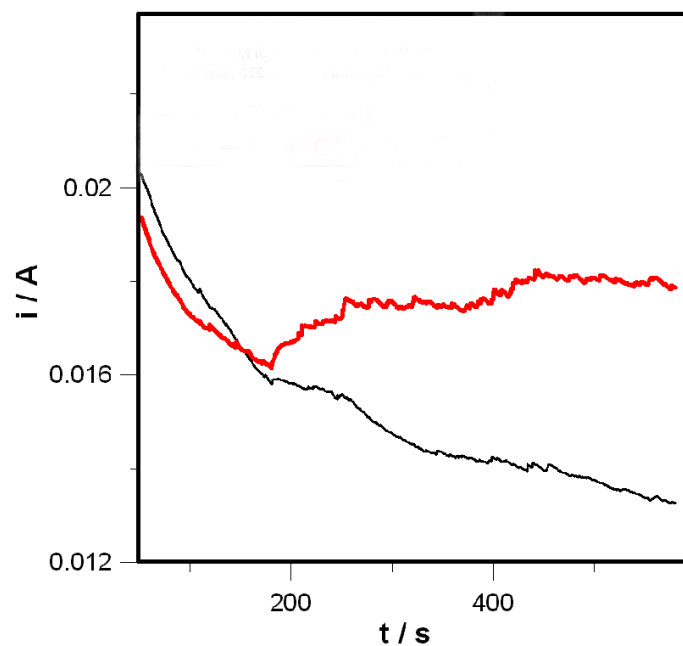


Figure S10. Current vs. Time plot with Pt/Nafion[®] (black line) and Pt/Nafion[®]/CoAPO5 (red line) as photoanode in 0.1 M K₂SO₄ solution. Light program: 0-180 s dark; 180-580 s light intensity of 1000 W/m². A constant potential of +1.6 vs. Ag/AgCl was applied.

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