Electronic Supplementary Material (ESI) for Energy & Environmental Science
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Stable electrocatalysts for autonomous photoelectrolysis of hydrobromic acid using single-junction solar cells

Supporting Information:

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Cost of Catalyst

At a price of approximately \$1500/oz, precious metals such as Rh or Pt would cost ~\$20/m^2 for a loading of 0.0432 mg/cm^2. For a price of \$20/m^2, assuming 1000 W$_{peak}$/m^2 (peak), and a 10% efficiency, the cost per peak Watt would be:

$$20\frac{\$}{m^2} * \frac{1}{1000\frac{W_{peak}}{m^2} * 0.1} = \$0.20/W_{peak}$$

Characterization of electrocatalyst after electrolysis

Following cyclic voltammograms for hydrogen evolution in fuming HBr, the electrocatalysts were characterized by X-ray diffraction.

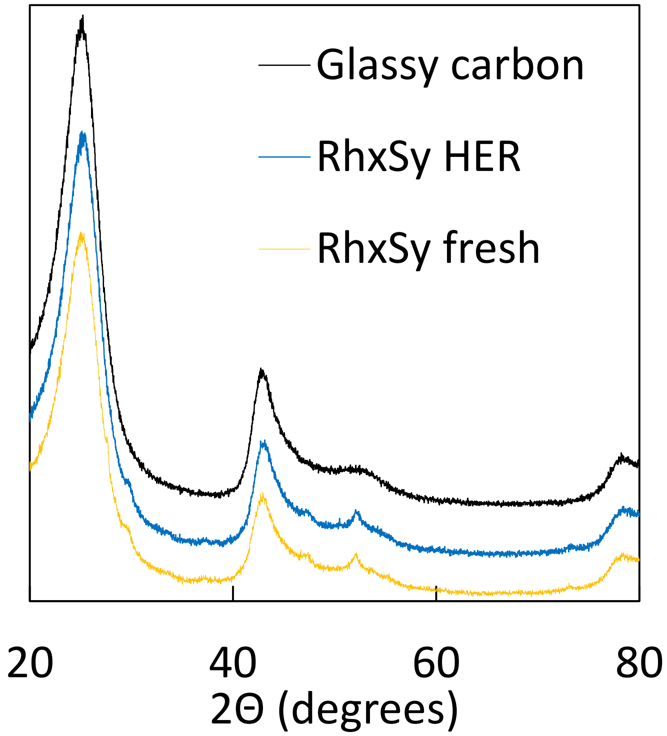


Figure S1: XRD of the glassy carbon support, fresh Rh_xS_y/C catalyst, and post-electrolysis Rh_xS_y/C catalyst.

The diffraction peaks of the Rh_xS_y/C catalyst did not appear to change significantly after hydrogen evolution and exposure to hydrobromic acid (Figure S1).

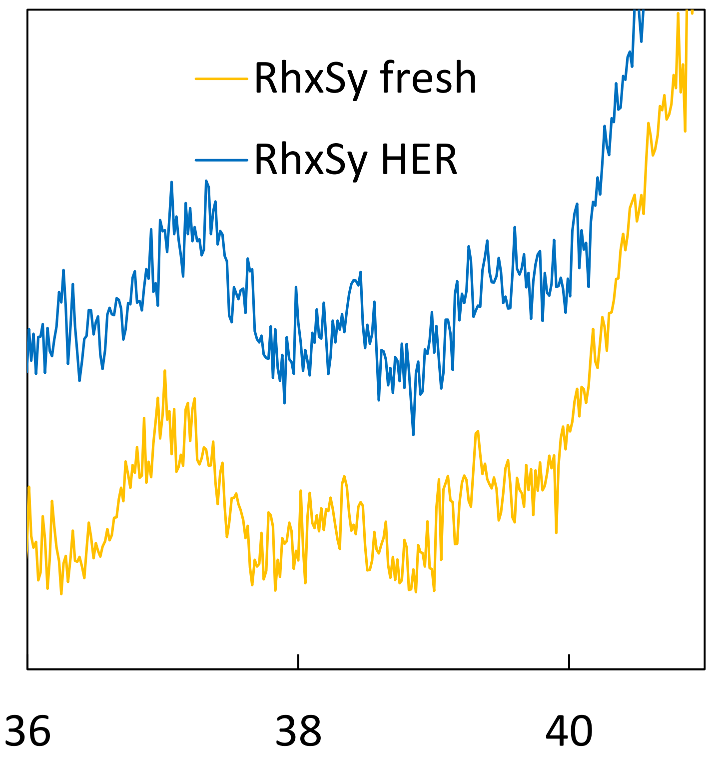


Figure S2: XRD of the fresh Rh_xS_y/C catalyst and post-electrolysis Rh_xS_y/C catalyst for the region where $Rh_{17}S_{15}$ can be identified.

A zoom in of the XRD indicates that the main XRD phase of the catalyst is $Rh_{17}S_{15}$ before and after electrolysis (Figure S2).[1]

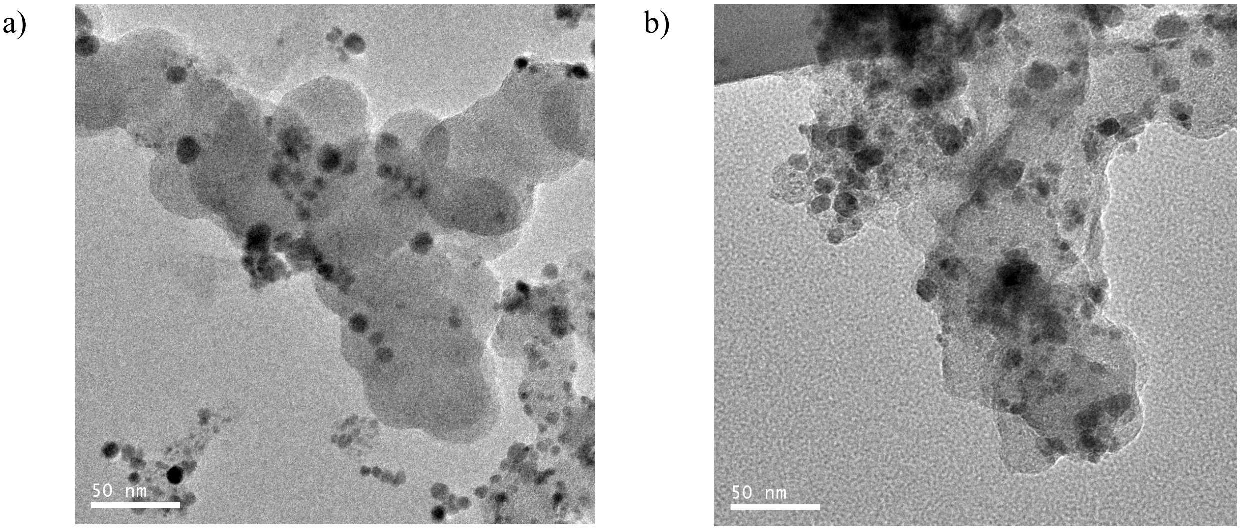


Figure S3: Transmission electron micrographs of a) the fresh Rh_xS_y/C catalyst and b) the Rh_xS_y/C catalyst after being used on the GaAs cathode for photoelectrolysis of HBr for two weeks

After continuous operation of the autonomous photoelectrochemical device, there did not appear to be any major changes in the dispersion, structure or catalyst particle size. The darker spots 5-20 nm are Rh_xS_y particles supported on the ~50 nm carbon spheres.

TEM-EDX of the fresh catalyst (Figure S4) shows the stoichiometry of the Rh_xS_y catalyst.

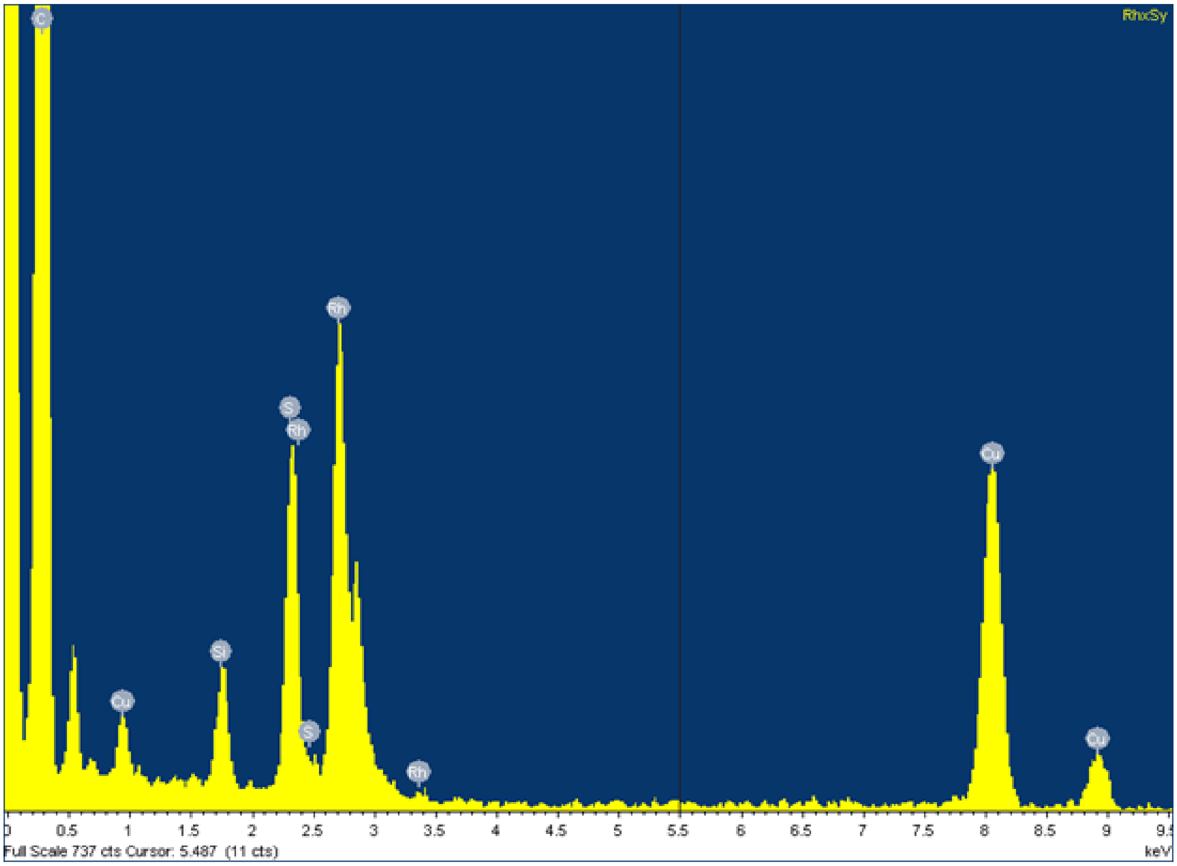
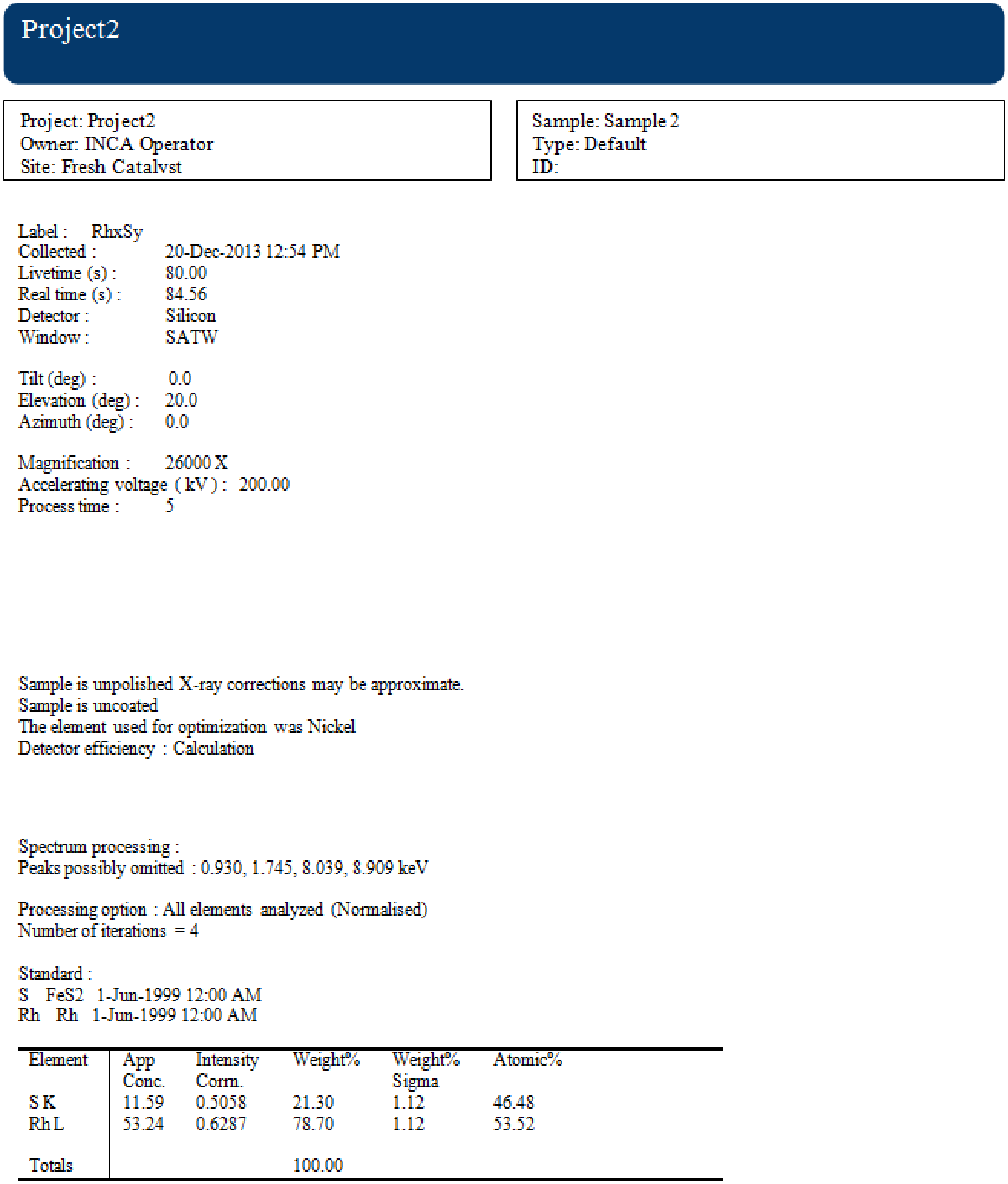


Figure S4: EDX of the fresh Rh_xS_y/C catalyst



Project2

Project: Project2
Owner: INCA Operator
Site: Fresh Catalyst

Sample: Sample 2
Type: Default
ID:

Label : RhxSy
Collected : 20-Dec-2013 12:54 PM
Livetime (s) : 80.00
Real time (s) : 84.56
Detector : Silicon
Window : SATW

Tilt (deg) : 0.0
Elevation (deg) : 20.0
Azimuth (deg) : 0.0

Magnification : 26000 X
Accelerating voltage (kV) : 200.00
Process time : 5

Sample is unpolished X-ray corrections may be approximate.
Sample is uncoated
The element used for optimization was Nickel
Detector efficiency : Calculation

Spectrum processing :
Peaks possibly omitted : 0.930, 1.745, 8.039, 8.909 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
S FeS2 1-Jun-1999 12:00 AM
Rh Rh 1-Jun-1999 12:00 AM

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
S K	11.59	0.5058	21.30	1.12	46.48
Rh L	53.24	0.6287	78.70	1.12	53.52
Totals			100.00		

Figure S5: EDX results from the fresh Rh_xS_y/C catalyst

The TEM-EDX of the catalyst after being using for photoelectrolysis is shown below:

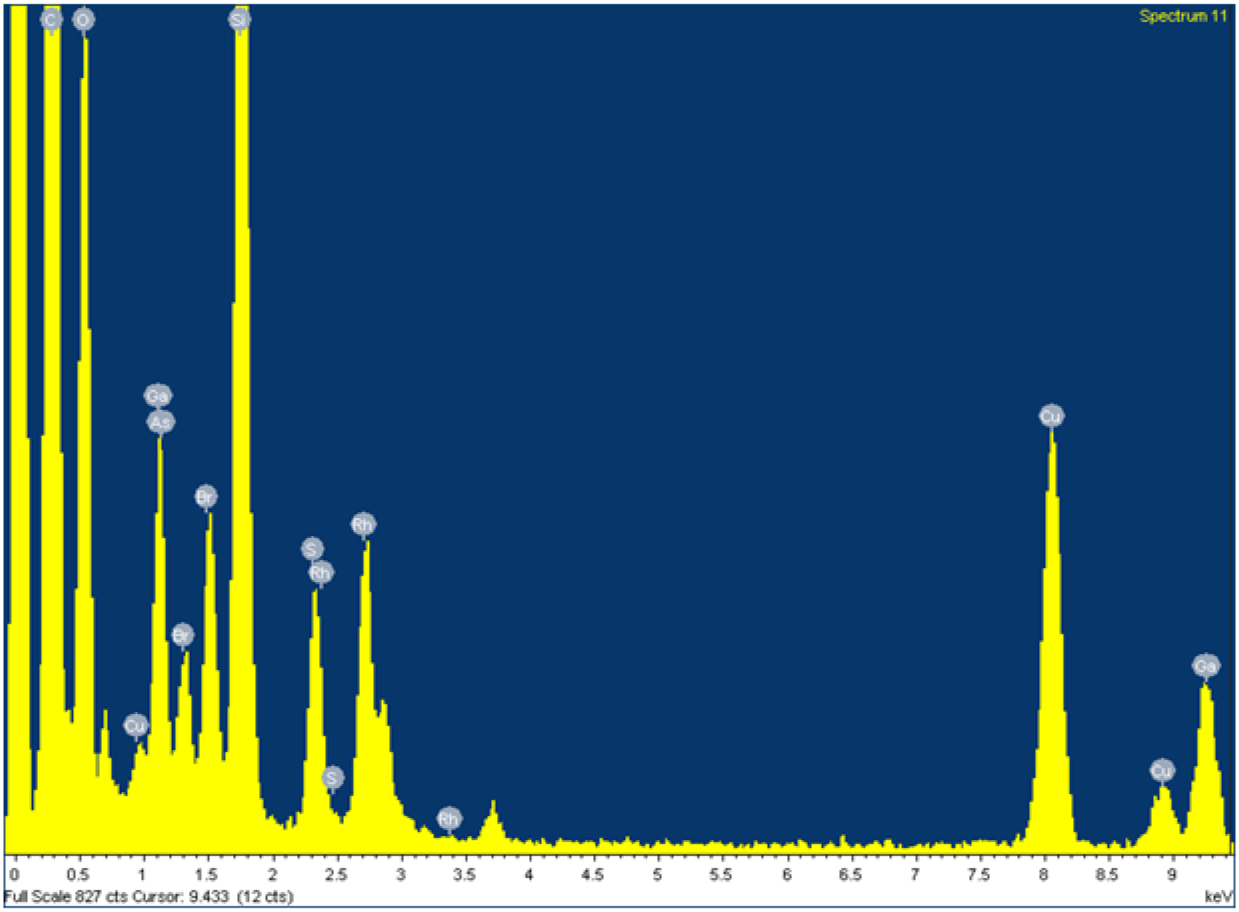
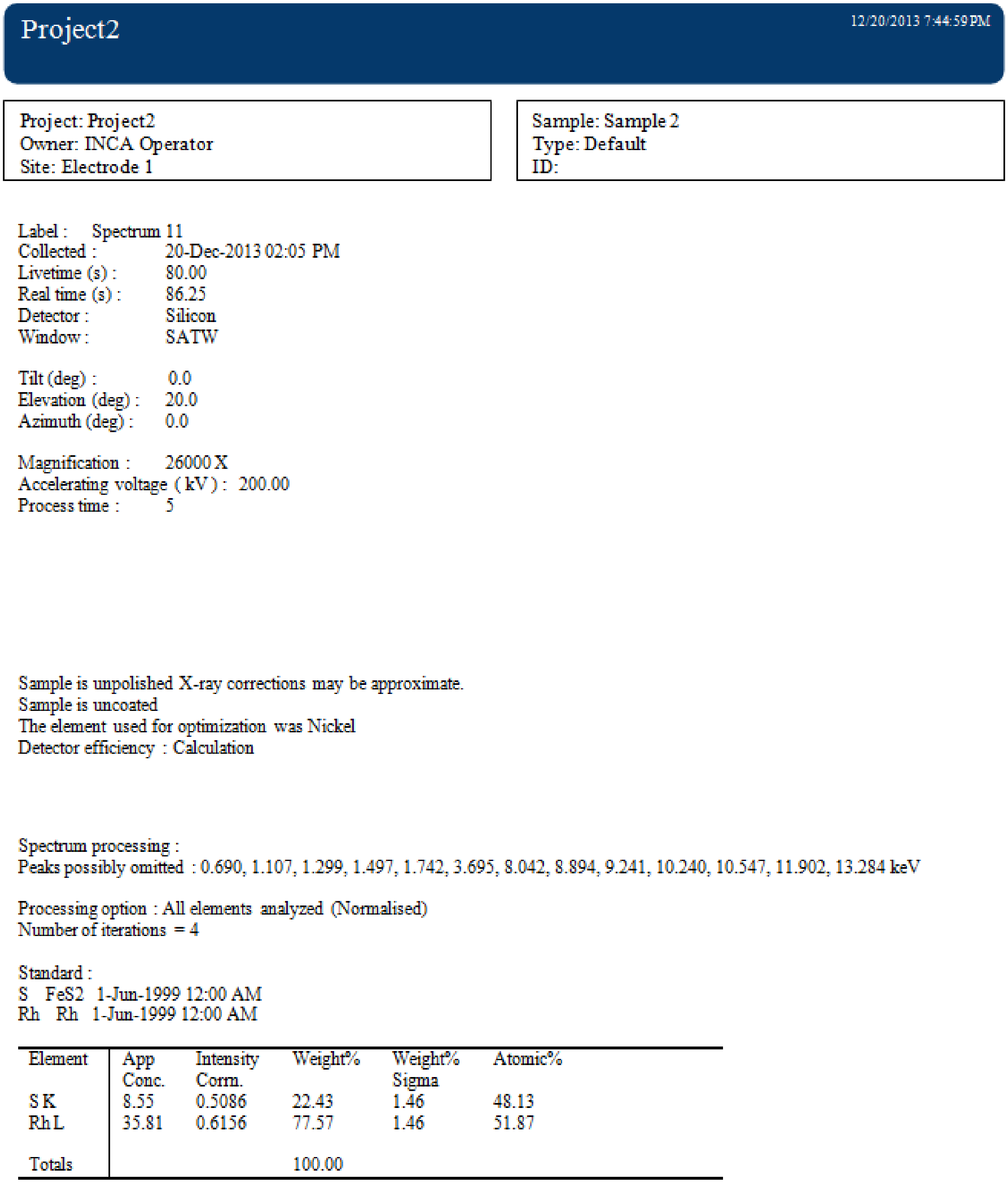


Figure S6: EDX results of the Rh_xS_y/C catalyst after being used for photoelectrolysis for two weeks.



Project2

12/20/2013 7:44:59 PM

Project: Project2
Owner: INCA Operator
Site: Electrode 1

Sample: Sample 2
Type: Default
ID:

Label : Spectrum 11
Collected : 20-Dec-2013 02:05 PM
Livetime (s) : 80.00
Real time (s) : 86.25
Detector : Silicon
Window : SATW

Tilt (deg) : 0.0
Elevation (deg) : 20.0
Azimuth (deg) : 0.0

Magnification : 26000 X
Accelerating voltage (kV) : 200.00
Process time : 5

Sample is unpolished X-ray corrections may be approximate.
Sample is uncoated
The element used for optimization was Nickel
Detector efficiency : Calculation

Spectrum processing :
Peaks possibly omitted : 0.690, 1.107, 1.299, 1.497, 1.742, 3.695, 8.042, 8.894, 9.241, 10.240, 10.547, 11.902, 13.284 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
S FeS2 1-Jun-1999 12:00 AM
Rh Rh 1-Jun-1999 12:00 AM

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
S K	8.55	0.5086	22.43	1.46	48.13
Rh L	35.81	0.6156	77.57	1.46	51.87
Totals			100.00		

Figure S7: EDX results from the Rh_xS_y/C catalyst after photoelectrolysis for two weeks.

The stoichiometry of the Rh:S is approximately that of $Rh_{17}S_{15}$. The catalyst is believed to be a mixed phase of $Rh_{17}S_{15}$, Rh_2S_3 and Rh_3S_4, and perhaps the high Rh concentration may be due to additional clusters of Rh. The error of the EDX measurement may also play a role. Overall, the stoichiometry is unchanged by photoelectrolysis.

Rh_xS_y/C on GaAs Samples

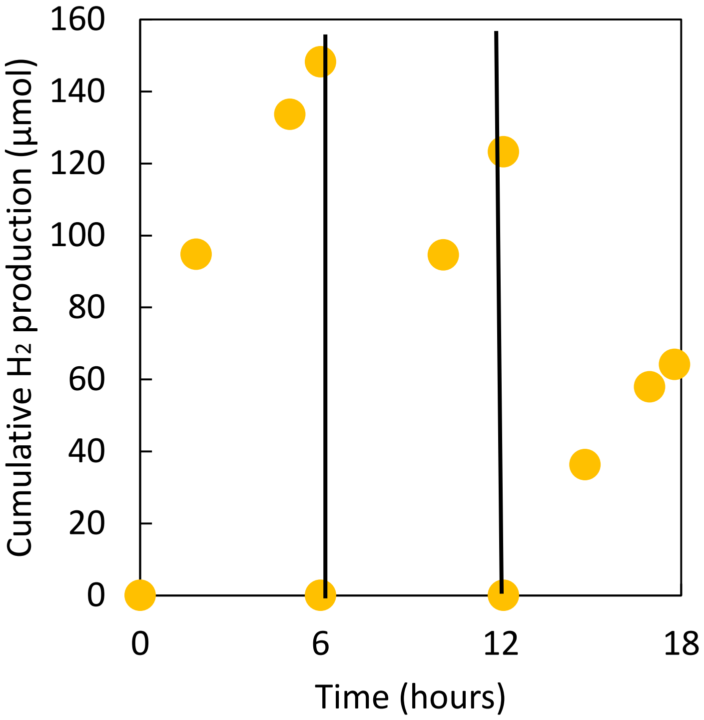


Figure S8: The effect of adding additional Rh_xS_y/C catalyst on efficiency of the device. At 6 and 12 hours the catalyst was re-added to the cathode of the GaAs cell. The activity was not recovered, indicating that the efficiency drop is not due entirely to the catalyst.

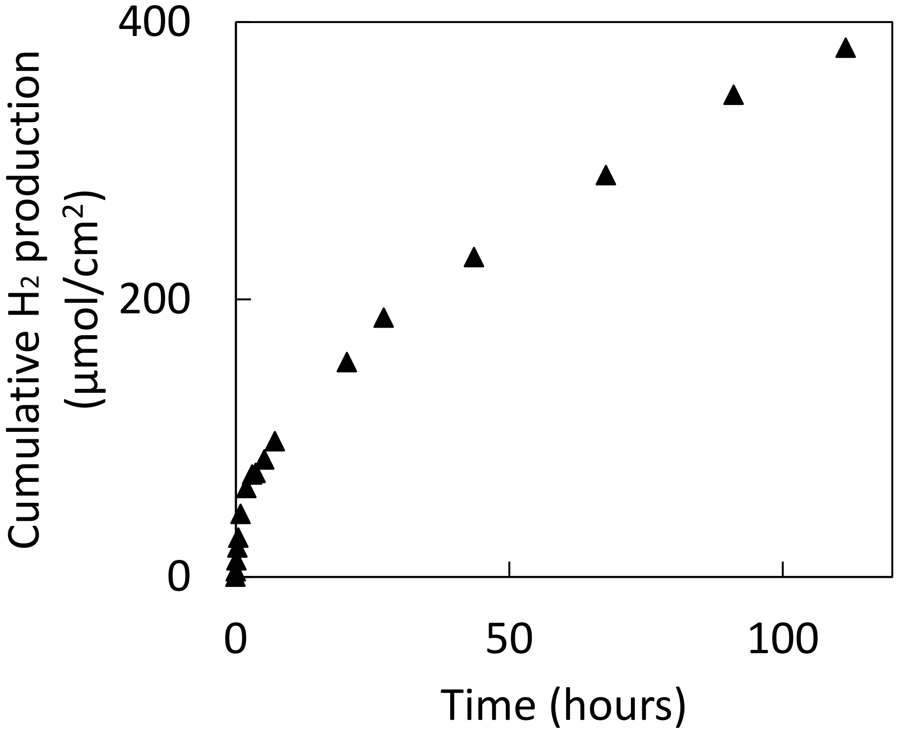
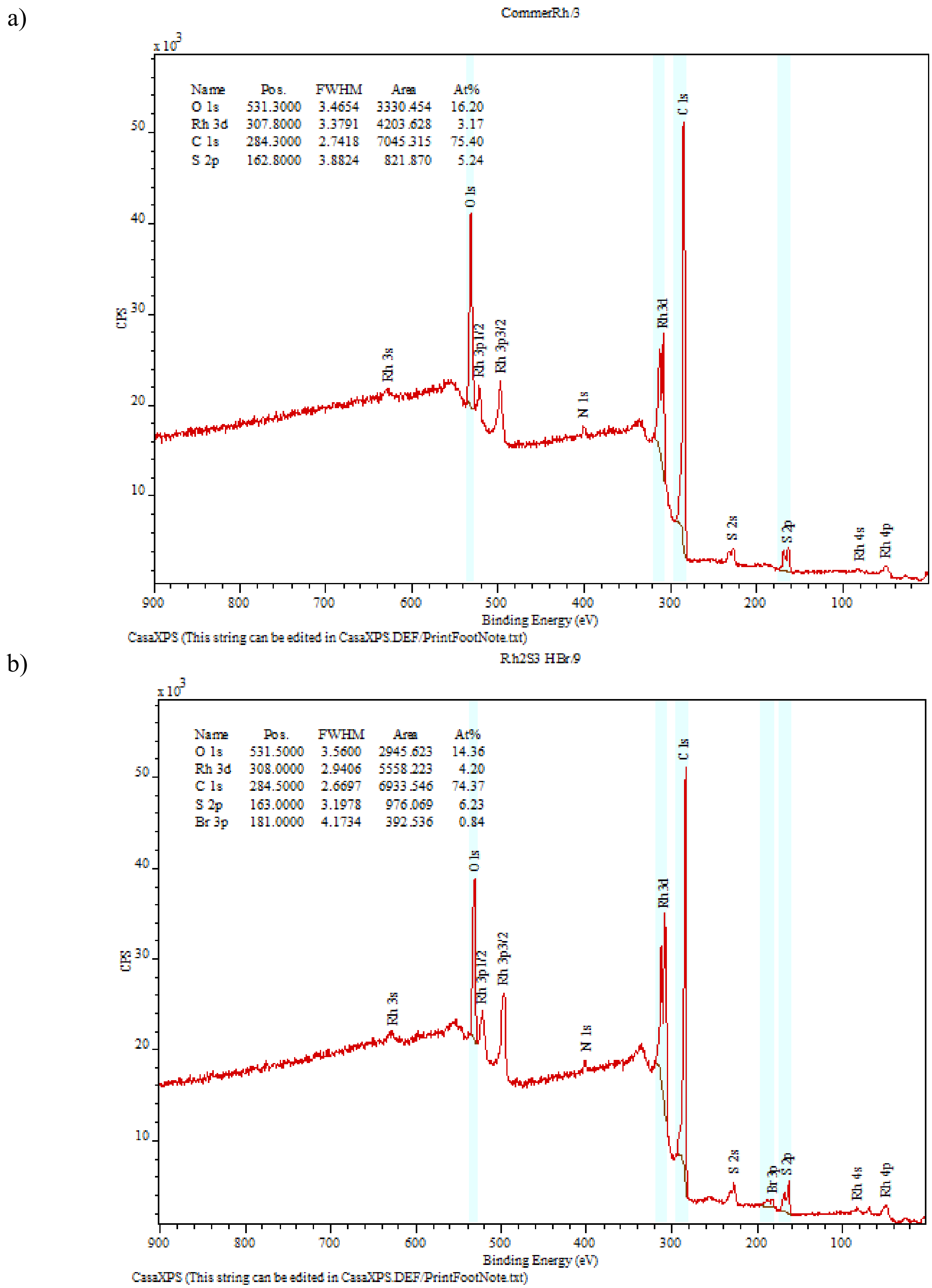


Figure S9: Rh_xS_y/C loaded onto the cathode of GaAs, illuminated at 15 mW/cm^2. H_2 production was measured using a Gas Chromatograph.



a)

Name	Pos.	FWHM	Area	At%
O 1s	531.3000	3.4654	3330.454	16.20
Rh 3d	307.8000	3.3791	4203.628	3.17
C 1s	284.3000	2.7418	7045.315	75.40
S 2p	162.8000	3.8824	821.870	5.24

b)

Name	Pos.	FWHM	Area	At%
O 1s	531.5000	3.5600	2945.623	14.36
Rh 3d	308.0000	2.9406	5558.223	4.20
C 1s	284.5000	2.6697	6933.546	74.37
S 2p	163.0000	3.1978	976.069	6.23
Br 3p	181.0000	4.1734	392.536	0.84

Figure S10: Rh_xS_y/C survey scan pre (a) and post (b) HBr exposure.

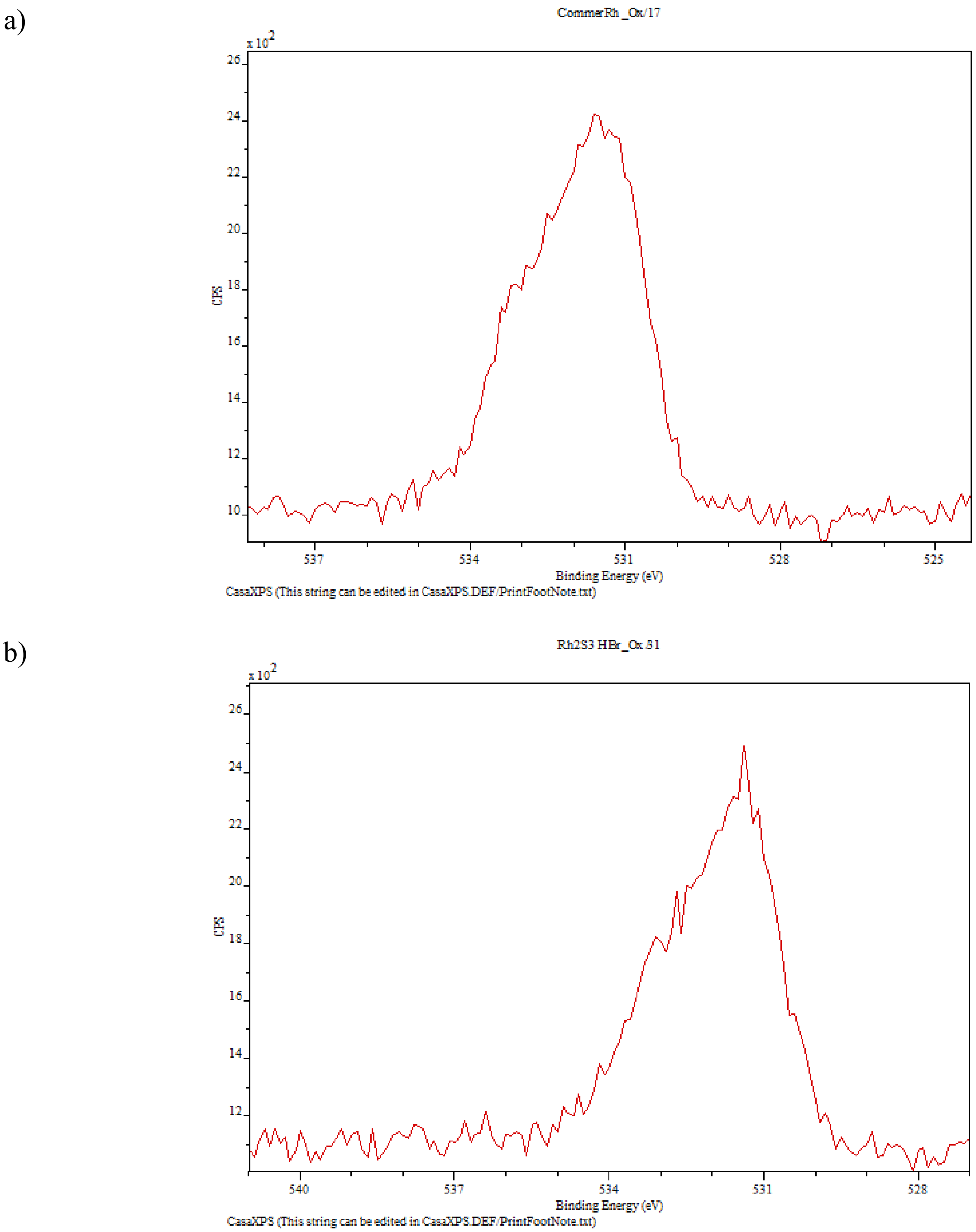


Figure S11: High resolution scans for the pre and post exposed Rh_xS_y/C catalyst. O fresh (a), O post (b).

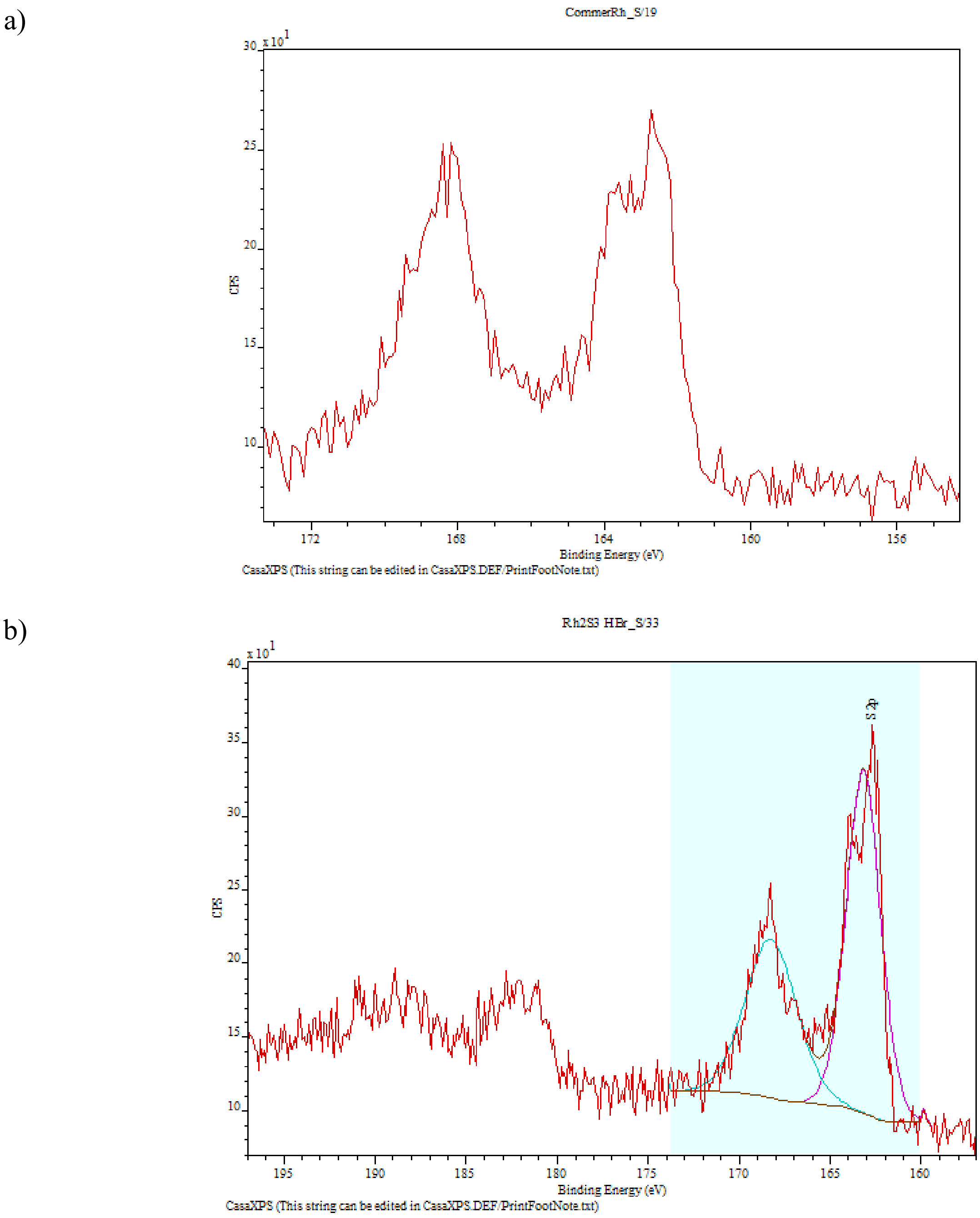


Figure S12: High resolution scans for the pre and post exposed Rh_xS_y/C catalyst. S fresh (a), S post (b).

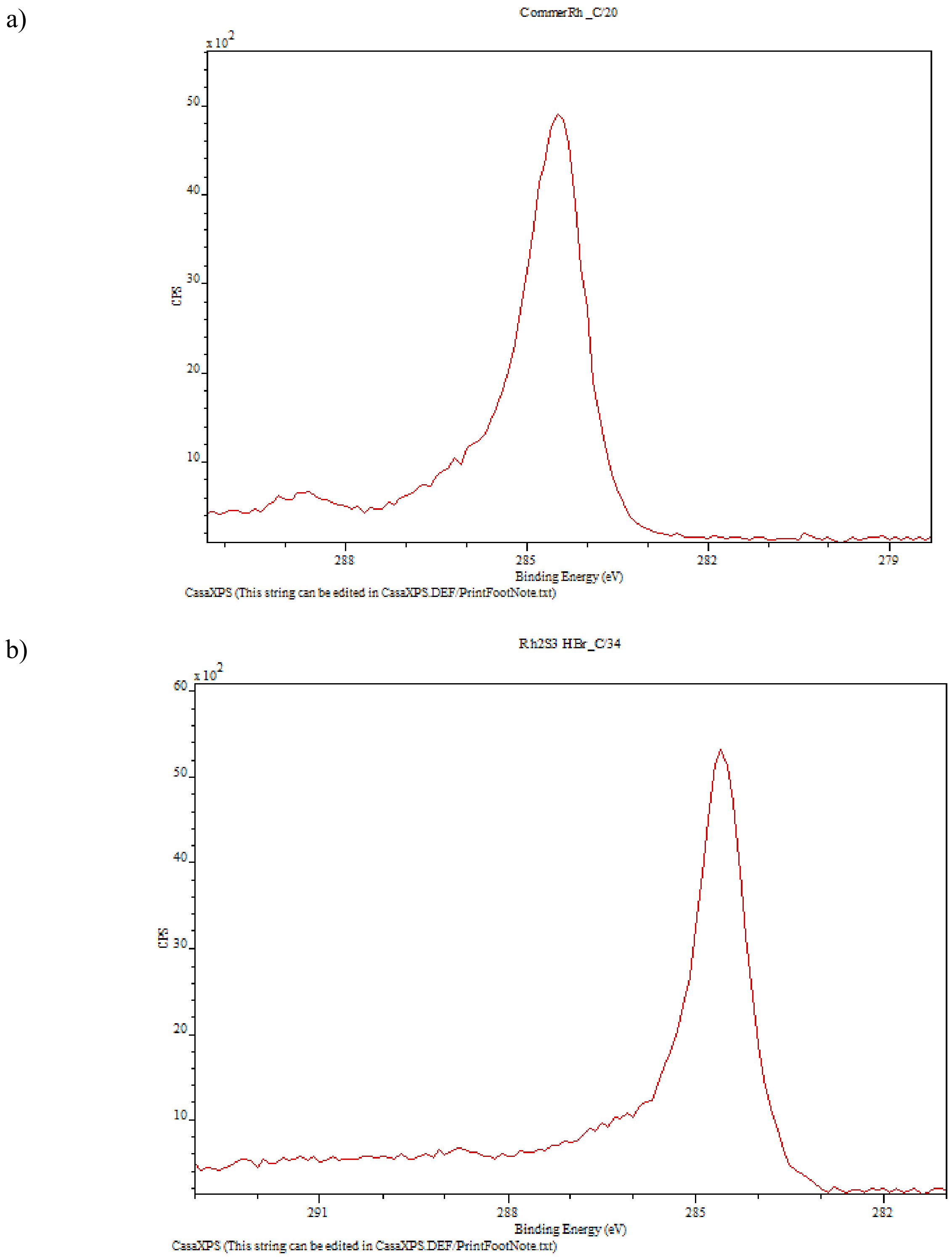


Figure S13: High resolution scans for the pre and post exposed Rh_xS_y/C catalyst. C fresh (a), C post (b).

Note that the binding energy ranges for the sulfur groups are different between post and pre exposure.

Experimental

Preparation of electrocatalysts for electrochemical testing

Electrocatalyst inks were formed by ultrasonicating 6 mg of commercial 30 wt% Pt/C (ETEK) or Rh_xS_y/C (BASF) in 1 mL 1:1 H_2O:IPA with 35 μL of 5% Nafion over 24 hours. The Nafion is used as a binder to hold the electrocatalyst in place on the substrate. The electrode substrates were prepared by spin coating a solution of PEDOT doped with PSS (PH500, Clevios) with 5 vol% DMSO onto an ITO substrate then drying at 120°C for 10 minutes, followed by immersion in ethylene glycol for 3 minutes to make the PEDOT:PSS water insoluble. Then the substrates were dried at 70°C for 1 hour under vacuum. The catalyst inks were dropped in three 8 μL aliquots onto the PEDOT coated ITO and dried at 110°C for 15 minutes before use. This resulted in a catalyst loading of 0.0432 mg/cm^2 by metal. Copper tape was used to contact the uncoated section of the ITO glass and used as electrical contact.

Electrochemical stability testing of Rh_xS_y/C and Pt/C

Fuming (48wt%) HBr (Sigma Aldrich) was used as the electrolyte with a BASi Ag/AgCl reference electrode and Pt counter electrode with no separator. Continuous cyclic voltammograms at 20 mV/s were used to evaluate the stability of the Pt/C and Rh_xS_y/C catalysts using a VSP Bio-Logic potentiostat. IR compensation was done using EC-Lab Software (PEIS).

Preparation of electrocatalysts for characterization

Rh_xS_y/C ink prepared as described above was dropped on a glassy carbon support and dried before use. An alligator clip was used to contact the glassy carbon support. The glassy carbon support allowed for X-ray diffraction measurements, unlike the powder following photoelectrolysis of HBr using the GaAs cell (due to the high Au and AuBr signals from the GaAs contact).

Characterization of Rh_xS_y/C after electrolysis

The Rh_xS_y/C deposited on glassy carbon was cycled from 0.5 to -0.3 V vs. Ag/AgCl for four hours at a scan rate of 100 mV/s in fuming HBr with a Pt counter electrode, and no separator. X-Ray Diffractograms were taken before and after cycling, and of the glassy carbon support alone, to detect any changes in crystallinity during electrolysis.

Electrochemical two-electrode testing

Fuming HBr was used as the electrolyte for a two electrode measurement, where the cathode consisted of Rh_xS_y/C on ITO prepared as described above, and the anode consisted of ITO coated with PEDOT:PSS with no additional catalyst. No separator was used and the cathode and anode were placed facing away from one another.

Chemical stability testing of Rh_xS_y/C

Dissolution product concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after exposure to 6 M HBr, 6 M HCl or 6M $HClO_4$ for 2 weeks.

Preparation of electrocatalysts on GaAs cells

GaAs cells were purchased from Millenium Co. To achieve a hydrophilic GaAs surface to facilitate spincasting of PEDOT:PSS, the anode of the GaAs was subjected to an O_2 plasma treatment for 1 minute at 30 mW, after which the PEDOT:PSS wetted the surface and gave much better coverage on the GaAs anode. PEDOT:PSS in 5 vol.% DMSO was coated on both sides of the GaAs cells by spincoating at 2500 rpm for 1 minute. The samples were then annealed at 120 °C for 10 minutes, then immersed in ethylene glycol for 3 minutes. To evaporate the remaining ethylene glycol the sample were heated under vacuum at 70 °C for 10 minutes. The catalyst inks were placed on the cathode side of the solar cell using the same method as described for the electrochemical preparation.

Testing of photoelectrolysis of HBr using GaAs p-n structures

The sample was held in a Pyrex™ glass vessel with the fuming HBr (Sigma Aldrich) electrolyte and illuminated using a Xenon lamp. The light intensity was measured using a silicon diode at the position of the device. Periodically a sample from the gas headspace is removed and the amount of hydrogen evolved measured by gas chromatography. The current density was calculated assuming 100% Faradaic efficiency of hydrogen production, using Equation 1,

$$\text{Current density} = \frac{\text{moles } H_2 \text{ x } 2\ {}^{e^-}\!/_{\text{mol}} \text{ x } 96500\ {}^{C}\!/_{e^-}}{\text{Time x device area}} \qquad (1)$$

The efficiency was calculated using Equation 2, where the open circuit voltage measured was 0.6V (after a cyclic voltammogram to form H_2 at the cathode and Br_2 at the anode). As the open circuit voltage will increase as we produce higher concentrations of hydrogen and bromine compared to HBr, the efficiency reported will underestimate the actual efficiency.

$$\text{Efficiency } (\%) = \frac{\text{Current density x Open circuit voltage}}{\text{Illumination density}} \text{ x } 100 \qquad (2)$$

Characterization of electrocatalyst after photoelectrolysis of HBr

TEM images of the fresh catalyst and the catalyst after continuous photoelectrolysis of HBr for two weeks (data not shown here) were taken using a XXX.

Characterization of Rh_xS_y/C and PEDOT:PSS catalyst after exposure to HBr

To test the effect of HBr on the surface composition of Rh_xS_y/C, the catalyst was exposed to 3 M HBr for 5 hours. Subsequently, high-resolution and survey XPS scans were collected using a Kratos Axis Ultra spectrometer. All binding energies were referenced to carbon black (conductive carbon) C 1s at 284.4 eV. The data was analyzed using CasaXPS.

References

1. S. Geller, *Acta Crystallogr.*, 1962, **15**, 1198.