Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting information

Selective production of hydrogen peroxide and oxidation of hydrogen sulfide in an unbiased solar photoelectrochemical cell

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Experimental Section

Electrodes preparation

Commercial single side polished n-Si wafers (P doped, 1.0 to 20.0 ω cm^{-1}, and 500 ± 25μm thickness, Topsil) were functionalized by surface p^+ doping and used as photoanodes. To create a surface p^+ doping, the n-Si wafers are subjected to a pre-deposition process in which the wafers are placed in an atmospheric pressure tube furnace in close proximity with BoronPlus planar diffusion sources (Techneglas, Perrysburg, OH, USA). The wafers are inserted into the furnace at 973 K, and the temperature is then ramped at 10 K min^{-1} to 1223 K where it remains for 10 min before cooling at 10 K min^{-1} back to 973 K where the wafers are extracted. The furnace is flushed with 5 standard litre per minute (SLM) nitrogen and 0.1 SLM oxygen during the process. After the pre-deposition process the boron phase layer is removed by soaking the wafers in buffered hydrofluoric acid (BHF) for 5 min. The dopant on the unpolished side of the wafer is removed simply by etching about 5 μm of the surface away in a Reactive Ion Etching (RIE) process (Pegasus, SPTS Technologies). The circular doped areas on the front of the wafer is created by a simple UV lithography process followed by a 3 μm deep reactive ion etch that leaves the doped areas as 3 μm tall mesas on the front of the wafer.

Commercial p-Si wafers (B doped, 2.2 ω cm, and 500 μm thickness) and those with surface fictionalization were used as photocathodes. p-Si wafers were processed to achieve a thin surface n^+ doping followed by successive deposition of 5 nm Ti and 100 nm TiO_2 protective layer according to reported procedures.[1,2] Pt catalyst was not deposited on the as-prepared $TiO^2/Ti/n^+p$-Si to ensure the high selectivity of the photoreduction reaction.

Photoelectrochemical Testing

Photoelectrochemical measurements were performed in a home-made two-compartment reactor with a quartz window. A Nafion 117 membrane (Dupont, conductivity: 0.083 S cm^{-2}, available acid capacity: 0.9 meq/g, thickness: 183 μm) was sandwiched between the cathodic and anodic compartments where anthraquinone-2-sulfonic acid sodium salt monohydrate (AQ, Aldrich, 97%) and potassium iodide electrolytes (KI, Aldrich, 99%) were stored, respectively. When the measurements were conducted in a three electrode system, platinum or carbon plates, Ag/AgCl or Saturated calomel electrode electrodes, and p-Si (or n-Si) electrode were used as the counter, reference, and working electrodes, respectively. When the experiment was carried out in a two electrode system, the counter electrode and the reference electrodes were joined together. Freshly prepared 0.1 M KI in 0.5 M H_2SO_4 solution and saturated AQ in 0.5 M H_2SO_4 solution were used as the electrolytes in the anodic or cathodic compartments, respectively. Both electrolytes were thoroughly purged with nitrogen before the start of any experiment, and during the entire duration of the experiment. Liner sweep voltammogram were swept at 50 mV S^{-1} using an Electrochemical Workstation (CHI660d) under solar AM 1.5 G illumination (100 mW cm^{-2}) using a Newport light source. The Faradaic efficiency for producing H_2O_2 and I_3^- was calculated based upon the real amount of H_2O_2 and I_3^- produced and that calculated from chronoamperometry test.

The solar-to-chemical (STC) energy conversion efficiency was roughly estimated for a two-electrode system using Pt/p^+n-Si photoelectrode in the presence of I^-/I_3^- (anodic compartment) and anthraquinone/anthrahydroquinone (cathodic compartment) redox couples without applied bias. The photochemical reaction proceeds according to the following equation:

$AQ + 2H^+ + 3I^- = H_2AQ + I_3^-$

and consists of two photochemical reactions:

$AQ + 2H^+ + 2e^- = H_2AQ$

$3I^- + 2h^+ = I_3^-$

Considering that the chemical potential of HI photoelectrolysis is 0.41 eV[3] and the reduction potential of AQ is 0.25 V more positive than that of proton, the efficiency was roughly estimated to be 1.1% based upon the following equation, where J_{sc} is the short-circuit photocurrent density (8 mA cm^{-2}), V is the chemical potential (0.16 V), η_F is the Faraday efficiency of the reaction (assuming that the Faraday efficiency is 90% for the anodic and cathodic reactions) and P_{total} is the solar energy input (100 mW cm^{-2}). We define this efficiency by assuming that the Pt/p+n-Si electrode showed stable photocurrent of 8 mA cm^{-2} during the reaction. Moreover, we simply assume that the chemical potential for the reaction is *ca.* 0.16 V without considering the influence of the redox species concentrations on it.

$$STC = \frac{J_{sc}(mA\ cm^{-2}) \times V \times \eta_F}{P_{total}\ (mW\ cm^{-2})}$$

Chemical reactions and characterizations

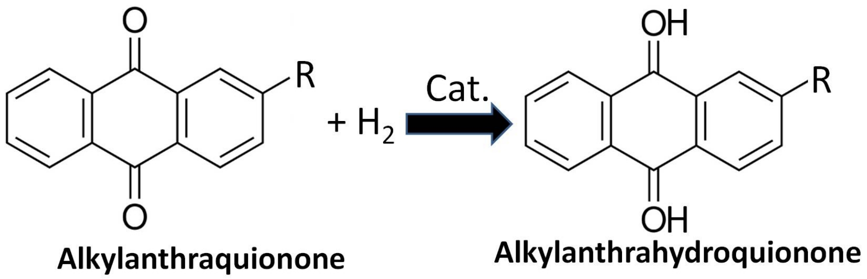
H_2S gas was produced by slowly dripping an acid solution to a well-grounded ferrous sulfide (FeS) powder in a tightly-sealed round bottomed flask with an outlet. The outlet of the flask is connected with a sintered-glass gas dispersion tube for the injection of H_2S into the anodic compartment of the reactor. Air from the gas line was bubbled to the H_2AQ solution in the cathodic compartment to produce H_2O_2. The amounts of I_3^- and H_2O_2 produced during the reactions were estimated using a titration method. Deionized water thoroughly purged with nitrogen was used to prepare all the titration solution. Freshly prepared 0.5% starch solution purged with nitrogen was used as the indicator. For I_3^- analysis, the pH of the sampled reaction solution was first adjusted to 3-4 with 0.1 M NaOH. Then 0.05 M $Na_2S_2O_3$ solution was used to titrate the I_3^- solution to calculate the amount of I_3^- produced according to the molar ratio of 1:2 for I_3^- and $S_2O_3^{2-}$. For H_2O_2 analysis, the solution was first bubbled with nitrogen and the pH of the sampled reaction solution was adjusted to 3-4 with 0.1 M NaOH. Then 0.01g of KI was added to the reaction solution and sealed in a container to allow for the complete reaction between H_2O_2 and KI to produce I_3^-. Finally, the amount of I_3- produced was analyzed using $Na_2S_2O_3$ solution. The amount of H_2O_2 produced was calculated based the amount of $Na_2S_2O_3$ used according the molar ratio of 1:2 for H_2O_2 and $S_2O_3^{2-}$. Note that the accurate measurement of the amount of sulfur produced was proven to be hard because of the difficulty in collecting all the sulfur powder due to its low amount and the adhesion of the sulfur powder to the absorption cell. In the meantime, we also understand that as the oxidation of H_2S by I_3^- can proceed almost completely according to the reaction $H_2S + I_3^- = 3I^- + 2H^+ + S$, we will try to give an more accurate estimate of the amount of S produced based upon the amount of I_3^- produced in our future study.

The possible generation of H_2 was qualitatively investigated by injecting a small amount of gas in the cathodic compartment to a gas chromatography (GC-2014, Shimazu) with a thermal conductivity detector (TCD). The crystal structure of the sulfur was investigated with X-ray diffraction on an X-ray diffractionmeter (Miniflex, Rigaku).

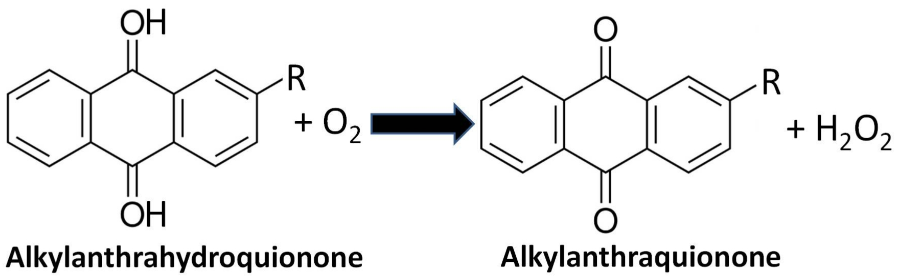
References

1. B. Seger, T. Pedersen, A. B. Laursen, P. C. K. Vesborg, O. Hansen and I. Chorkendorff, *J. Am. Chem. Soc.*, 2013, 135, 1057-1064.
2. B. Seger, A. B. Laursen, P. C. K. Vesborg, T. Pedersen, O. Hansen, S. Dahl and I. Chorkendorff, *Angew. Chem. Int. Edit.*, 2012, 51, 9128-9131.
3. T. Yang, H. Wang, X. M. Ou, C. S. Lee and X. H. Zhang, Adv. Mater., 2012, 24, 6199-6203.

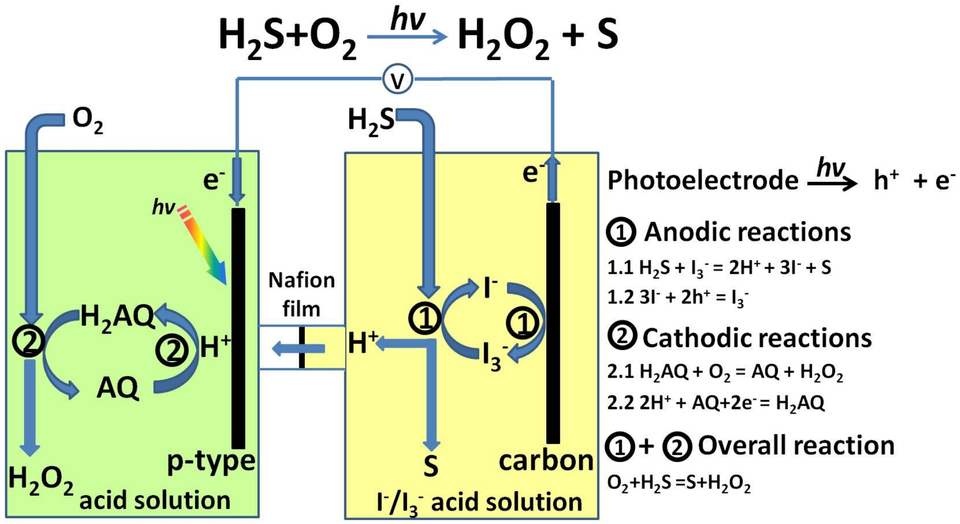
Step 1: Alkylanthraquionone hydrogenation



Step 2: H_2O_2 formation via autooxidation



Scheme S1. Industrial production of H_2O_2 using anthraquionone autooxidation approach.



Scheme S2. Integrated photoelectrochemical-chemical reaction pairs for selective and unbiased production of H_2O_2 and S from H_2S and O_2 on p-type electrode.

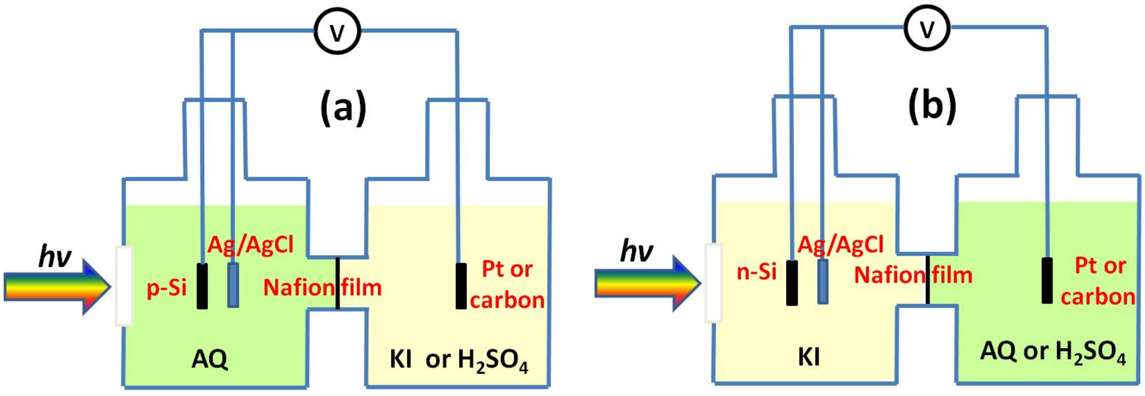
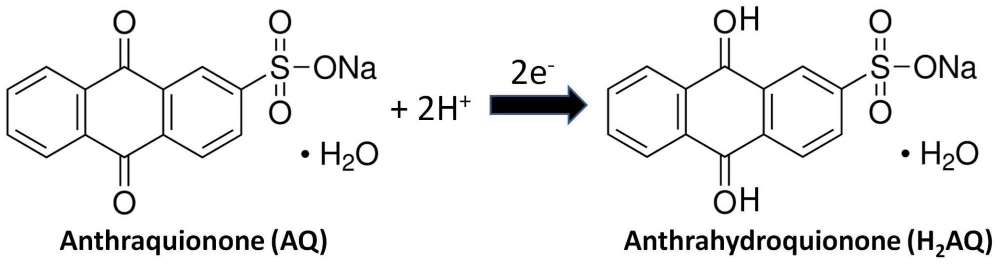
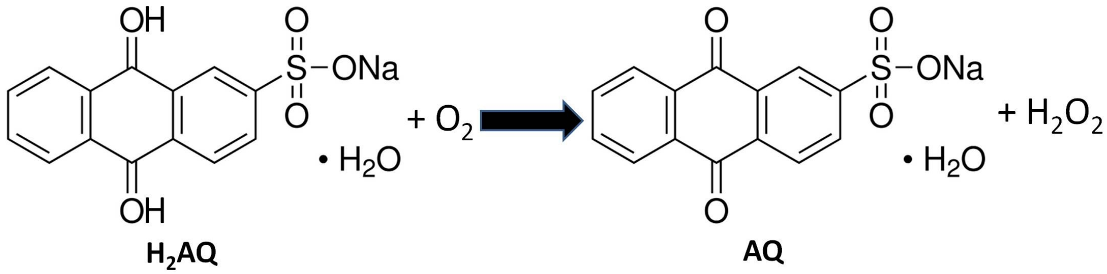


Figure S1. Schematic illustration of the setups using (a) p-Si or (b) n-Si photoelectrodes for photoelectrochemical measurement. A Nafion film is sandwiched between the two compartments.

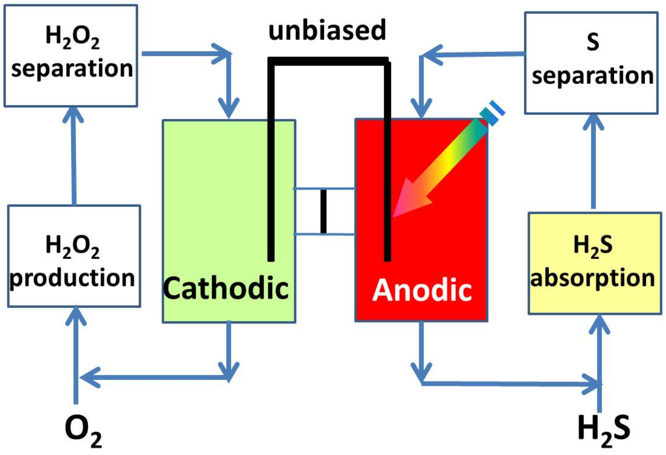
Step 1: Photoreduction of AQ to H_2AQ



Step 2: H_2O_2 formation via autooxidation



Scheme S3. H_2O_2 formation via the photoelectrochemical-chemical coupled reactions.



Scheme S4. Schematic illustration on the selective production of H_2O_2 and S from O_2 and H_2S on n-type electrode in the real practice.

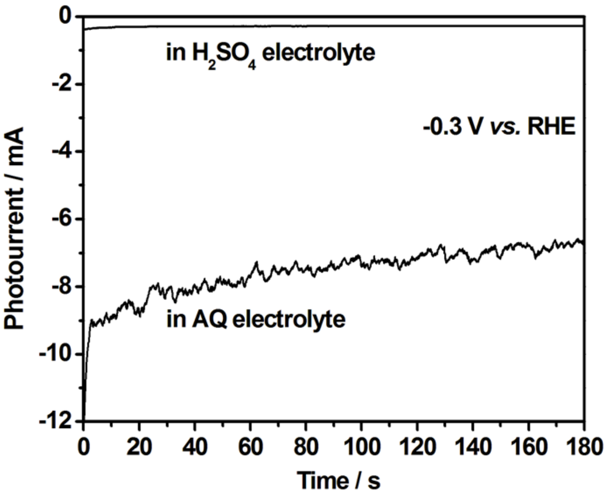


Figure S2. Chronoamperometry at an applied potential of -0.3 V *vs.* RHE on p-Si electrode in H_2SO_4 or AQ electrolyte in a three electrode system. It is evident that the photocurrent observed in an AQ electrolyte is much higher than that obtained in the H_2SO_4 electrolyte.

Figure S3. Picture showing the generation of H_2AQ in the cathodic compartment (left) after chronoamperometry test. A three electrode system was used during the measurement and H_2SO_4 solution was used in the anodic compartment.

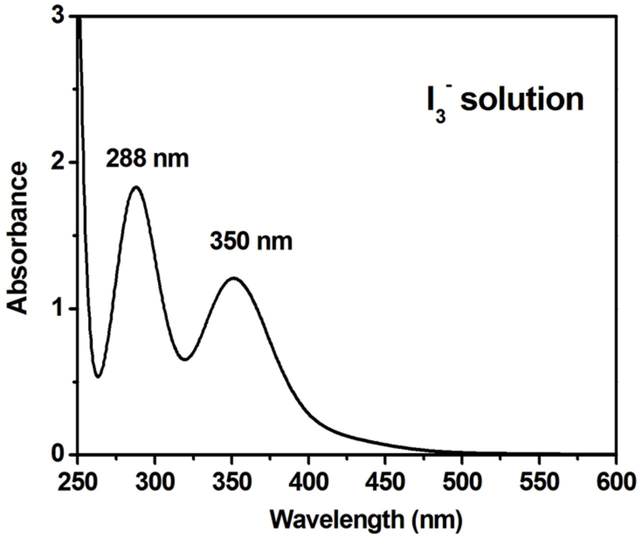


Figure S4. UV-Vis spectrum of the solution in the anodic compartment after current-potential scan. The two peaks at 288 and 350 nm indicate the generation of I_3^-, which is in agreement with the color change of the solution.

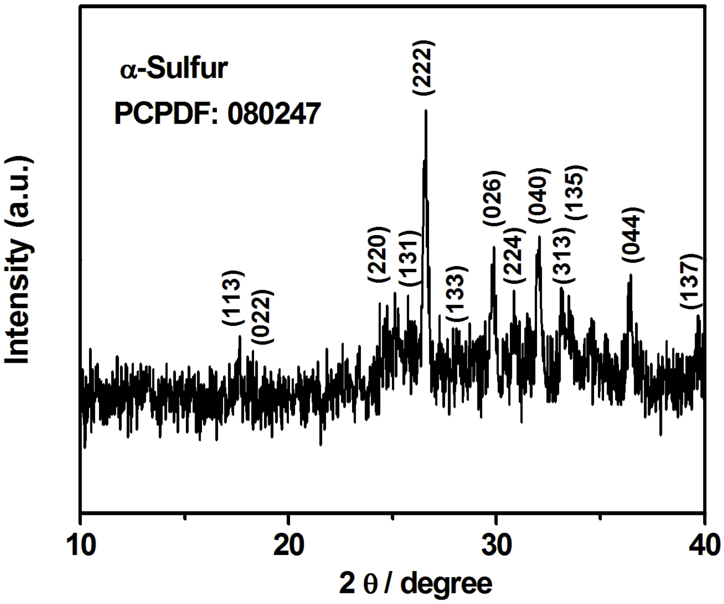


Figure S5. X-ray diffraction patterns of the as-obtained S powder.

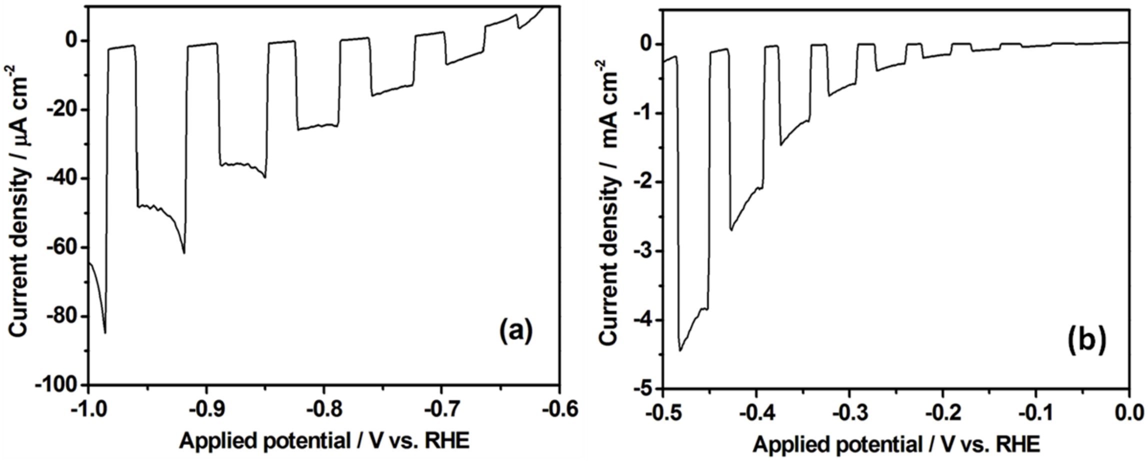


Figure S6. Bias current-voltage curves in a two electrode system on p-Si electrode. The cathodic compartment contained saturated AQ acidic solution and the anodic compartment contained (a) 0.5 M H_2SO_4 solution, and (b) 0.1 M KI acidic solution. Note the y-axis scale of a is µA cm^{-2}, while that for b is mA cm^{-2}.

Figure S7. Picture showing the simultaneous generation of I_3^- and H_2AQ in the anodic and cathodic compartments after chronoamperometry test on Pt/p$^+$n-Si.

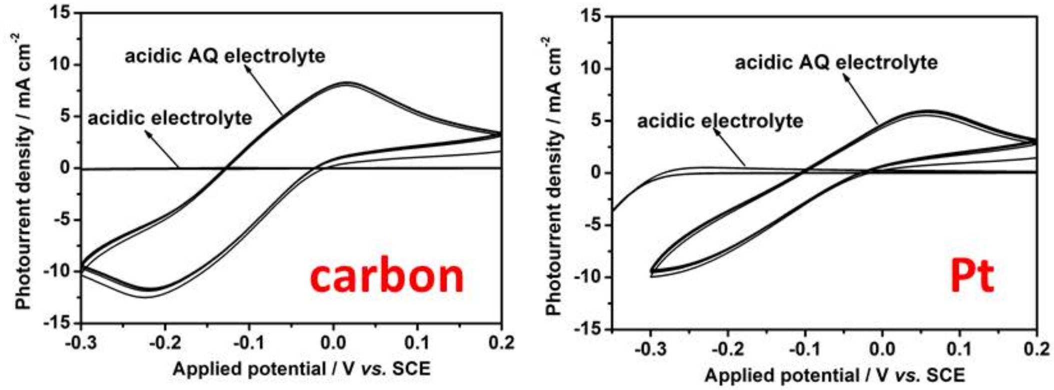


Figure S8. Cyclic voltammograms of carbon and Pt electrodes. Saturated acidic AQ solution or H_2SO_4 solutions were used as the electrolytes. A scan rate of 50 mV S^{-1} was used. These results indicate the carbon plate is a better catalyst than Pt for catalyzing AQ reduction. Moreover, carbon cannot catalyze H_2 production at low applied potentials as tested in the presence of H_2SO_4 solution.