Supporting Information – Park et al., Caltech

Preparation of BiO\textsubscript{x}-TiO\textsubscript{2} and stainless steel couple

A Ti metal sheet (Ti-Gr.2 sheet, 0.50 mm thick) was cleaned using SiC sandpaper (120 to 240 grit) before coating with substrates. The coating process typically consists of a pre-coat containing Ir and Ta (Ir:Ta = 0.67:0.33 mole ratio), a sealing coat comprising SnO\textsubscript{2} doped with Bi (Sn:Bi = 0.9:0.1), a slurry coating comprising TiO\textsubscript{2} and optionally doped with Bi (Ti:Bi = 0.96:0.04), and an overcoat essentially comprising the oxides of Ti and Bi (Ti:Bi = 0.9:0.1). Each step of coating requires a specific heat treatment regime with different temperatures and times. The anode-cathode couple is composed of a single anode with an active area of contact the electrolyte (10.0×1.2×2.0 cm) and two pieces of the same-sized SS cathode (Hastelloy C-22) faced the both sides of the anode with a distance of separation of 2 mm.

![Figure S1. PV performance as a function of solar radiation. Theoretical energy conversion efficiency (TE) of the employed PV is around 4.5% and actual efficiency (AE) is about 3%.](image)

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Figure S2. Effect of sodium chloride concentrations on the degradation rate \( (k) \) of phenol (■) and the current efficiency for hydrogen production (○) in 50 mM Na\(_2\)SO\(_4\). For comparison, effect of 50 mM NaCl without Na\(_2\)SO\(_4\) was also shown for \( k \) (□) and hydrogen production (○). The current efficiency for hydrogen = (number of H\(_2\) molecules × 2) / (number of electrons) × 100\%. 
Figure S3. The relative effects of organic reductants on H₂ production rates. 1: maleic acid, 2: oxalic acid, 3: phenol, 4: catechol, 5: salicylic acid, 6: 2-chlorophenol, 7: 4-chlorophenol. The sidebars refer to hydrogen production rates of 5 × 10⁻⁶ mol/min.

A Brief Description of a 20 L Hybrid PV- Electrochemical Reactor (Figure S4)

For application to pilot or sub-pilot scale, a batch reactor of 20 L-size was prepared where 5 anodes (each, 800 cm²) and 6 cathodes of the same size are arranged to alternatively face each other. At 60W (3V×20A) of power supply, carbon dioxide starts being released after 20 min and the rate of hydrogen production reaches ca. 3.5×10⁻³ mol/min along with hydrogen energy efficiency of 30%. The half life time of 1 mM phenol in a total volume of 20 L is < 2 min. Based on this operation condition, we can estimate the required PV areas with different efficiencies (PV% = P_{PV,max}/(I_{S,0} × PV area) × 100) for treating variable capacity of water/wastewater contaminated with 1 mM phenol. It is clear water treatment capacity is strongly related to the PV area and efficiency. For example, treatment of 16 metric tons of water (i.e., 1.6 kg phenol) daily (i.e., operation for 9 h/day) needs a 62 m² PV panel operating at 10% efficiency. Currently, the PV efficiencies are being improved and the 10% efficiency is most readily available. In addition,
hydrogen is obtained as a potentially useful byproduct. Hydrogen production rates are affected both by the water treatment capacity and H₂ energy efficiency. Small-scale reactors are usually better than large reactors for the energy efficiency. At a H₂ energy efficiency of 60%, the treatment of 16 tons of water with a PV of 10% efficiency will yield around 1 kg of H₂ daily.

Figure S4. (a) A DC-powered electrochemical oxidation of phenol to carbon dioxide and generation of hydrogen in a sub-pilot scaled reactor (20L) at E_{cell} = 3V and I_{cell} = 20A. [phenol]₀ = 1 mM. (b) Correlation between water treatment capacity and required PV area with different efficiencies. (c) Effects of water treatment capacity on the amount of hydrogen obtainable with different energy efficiencies at a PV of 10%. (b) and (c) were estimated based on the operation of the sub-pilot scaled reactor. Capacity of water treatment = 20L/h (1mM phenol) at 60W (3V×20A); daily solar utilization time (working hours) = 9 h (9 am to 6 pm, California); average solar energy input = 1100 W m⁻²; PV-driven energy output = 1100 W/m² × PV max efficiency (PV%) × application factor (0.7).