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

Supplementary Information for

Solar Photoelectrochemical Synthesis of Electrolyte-free H_2O_2 Aqueous Solution without Needing Electrical Bias and H_2

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Total number of pages: 6

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Table S1. Comparison of the previous studies of photoelectrochemical (PEC) production of H_2O_2.

Anode	Cathode	Electrolyte	Applied bias	H_2O_2 concentration (mM)	FE (%)	Durability (h)	Ref.
$WO_3/BiVO_4/Al_2O_3$	Pt	0.5 M $KHCO_3$	1.5 V of E_{cell}	2.5	65	0.5	[1]
$WO_3/BiVO_4$	Pt	0.5 M $KHCO_3$	1.5 V of E_{cell}	~2	30	1	[2]
WO_3	Co^{II}(Ch)	Seawater (0.55 M NaCl)	No bias	~48	-	24	[3]
$WO_3/BiVO_4$	Au	2 M $KHCO_3$	No bias	0.25	-	-	[4]
FeOOH/$BiVO_4$/GIGS	C_3N_4/rGO	0.1 M KPi	No bais	~6	-	3	[5]
Pt	BH_4/NiO	0.2 M KCl + 20mM MOPS	0.42 V vs. RHE	0.97		25	[6]
Pt	BH_4/NiO	0.1 M $TBAPF_6$ + 0.5 M acetic acid + 0.2 M BAQ	-0.2 V vs. RHE	~4	84-95	3	[7]
h-TNR	CNT/a-CP	0.1 M Na_2SO_4	0.7 V of E_{cell}	0.13	90-100	10	[8]
P-Mo-$BiVO_4$	AQ on CNT	1 M $NaHCO_3$	1.0 V vs. RHE No bias	4.2 0.6	Anode: 55 Cathode: 100	100	[9]
RuO_x/TNR	AQ on graphite	Anode: 1 M H_2SO_4 Cathode: 1 M KOH	No bias	~80 (**electrolyte-free**)	90	100	**This work**

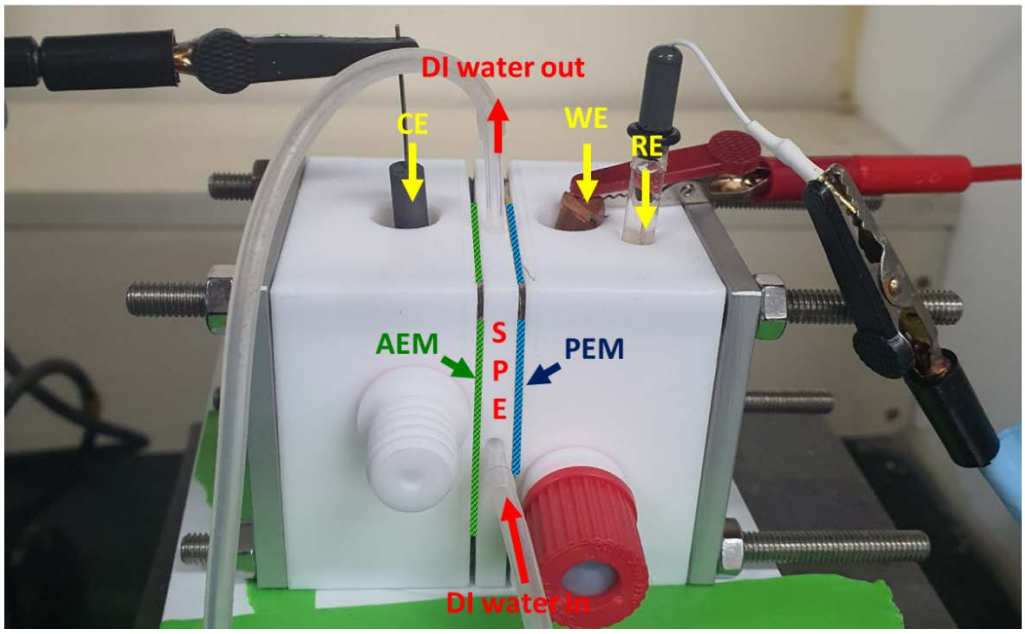


Figure S1. Photo of three-compartment-stack cell for pure H_2O_2 solutions production.

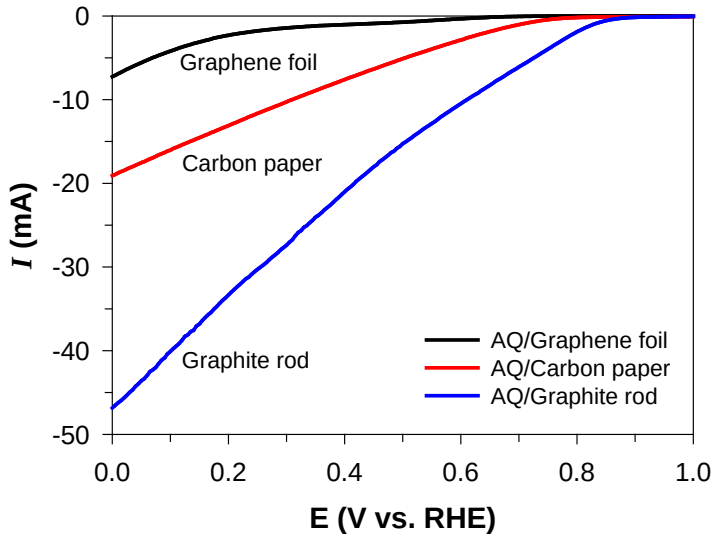


Figure S2. Linear sweep voltammograms (LSVs) of various carbon-based substrates anchored with AQ in 1 M KOH purged with O_2 gas.

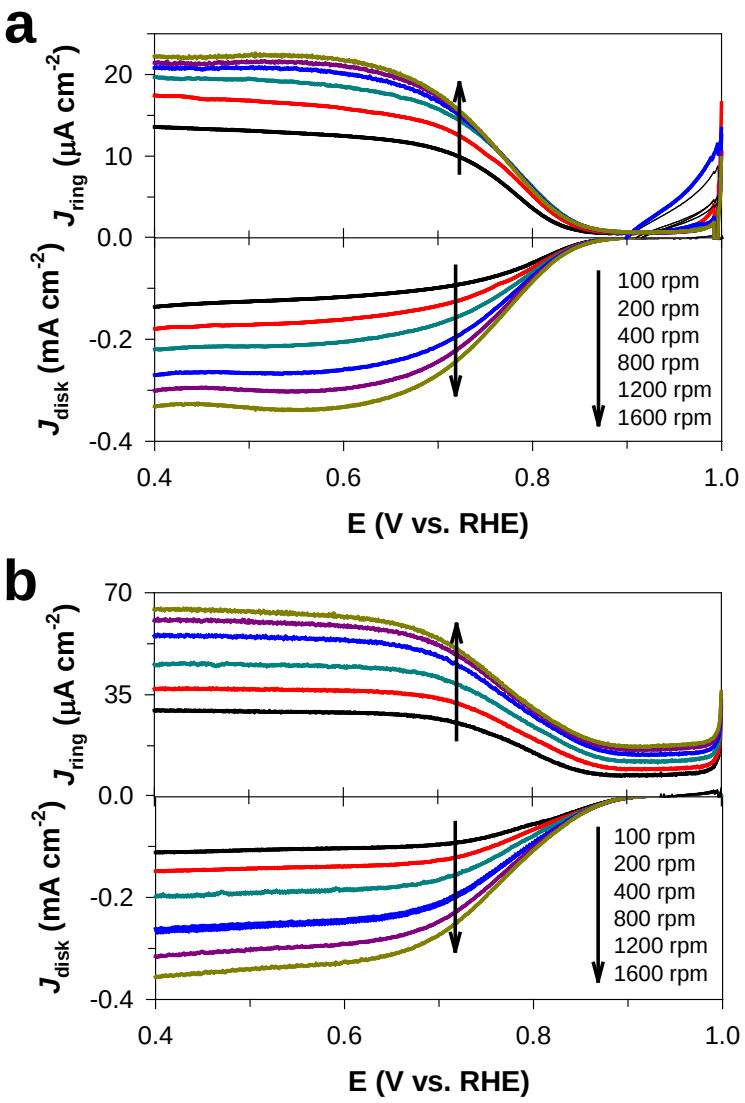


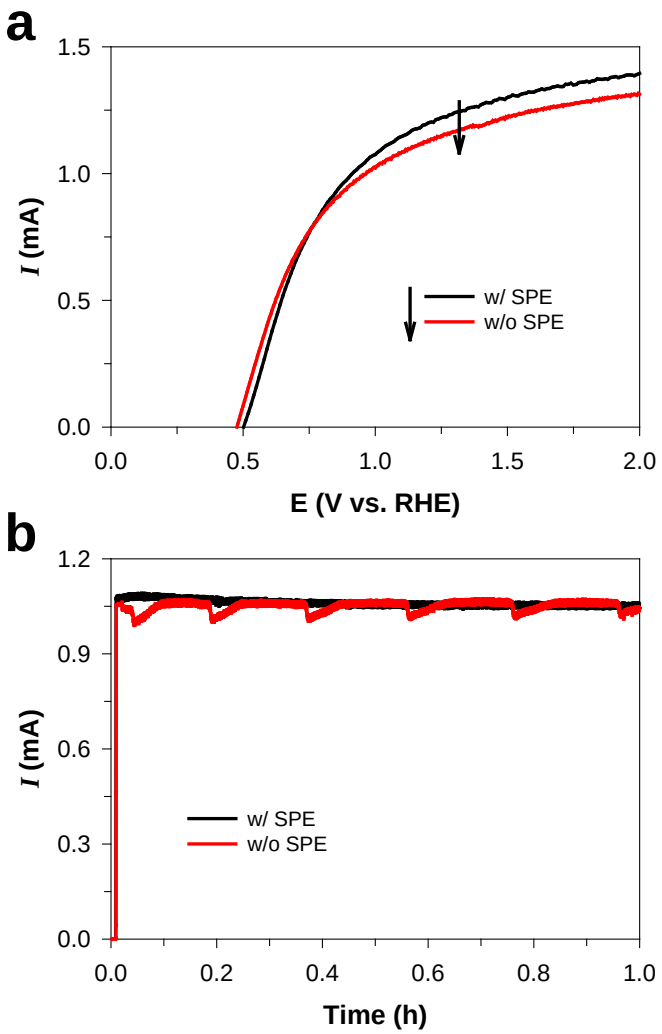
Figure S3. Rotation speed-dependent RRDE current-potential curves of (a) bare graphite rod (G) and (b) anthraquinone-anchored graphite rod (AQ/G) in 0.1 M KOH purged with O_2 gas.

The electron transfer number (n) and HO_2^- selectivity (%) were estimated based on the following equations:

$$n = \frac{4 \times I_{Disk}}{I_{Disk} + \frac{I_{Ring}}{N}}$$

$$\%(HO_2^-) = \frac{200 \times \frac{I_{Ring}}{N}}{I_{Disk} + \frac{I_{Ring}}{N}}$$

Where I_{Disk}, I_{Ring}, and N refer to disk current, ring current, and current collection efficiency of the Pt ring (0.424).



	pH (w/ SPE)		pH (w/o SPE)	
	Initial	Final	Initial	Final
Photoanode compartment	0.13	0.15	0.13	0.19
Cathode compartment	13.67	13.60	13.67	13.40
H_2O_2 solution (Middle compartment)	5.9	6.80	5.9	10.90

Figure S4. (a) Linear sweep voltammograms (LSVs) and (b) photocurrent-time profiles of the configuration using RuO_x/TNR and AQ/G electrodes in the presence and absence of SPE in the middle compartment. The table shows pH of the solution in anode, cathode, and middle compartments after 1 h PEC reaction in the presence and absence of SPE. The initial pH of 1 M H_2SO_4 and 1 M KOH in photoanode and cathode compartments were 0.15 and 13.60, respectively.

Solar to Fuel (H_2O_2) calculation formula

Solar to H_2O_2 energy conversion efficiency for the external bias-free experiments was calculated using the following equation:

$$\text{Solar to } H_2O_2 \text{ energy conversion efficiency (\%)} = \frac{\text{Output energy as } H_2O_2 \text{ produced}}{\text{Energy of incident solar light}} \times 100 = \frac{\Delta H \times \text{Amount of } H_2O_2 \text{ produced}}{P_{in} \times S} \times 100$$

where ΔH, amount of H_2O_2 produced, P_{in}, and S refer to the enthalpy change from the equation ($2H_2O + O_2 \rightarrow 2H_2O_2$; 98.3 $kJ \cdot mol^{-1}$), mol H_2O_2 per s, intensity of incident solar light (100 $mW \cdot cm^{-2}$), and irradiation area (1 cm^2), respectively.

Reference

1 K. Fuku, Y. Miyase, Y. Miseki, T. Gunji and K. Sayama, *RSC Adv.*, 2017, **7**, 47619-47623.
2 K. Fuku and K. Sayama, *Chem. Commun.*, 2016, **52**, 5406-5409.
3 K. Mase, M. Yoneda, Y. Yamada and S. Fukuzumi, *Nat. Commun.*, 2016, **7**, 11470.
4 K. Fuku, Y. Miyase, Y. Miseki, T. Funaki, T. Gunji and K. Sayama, *Chem. Asian J.*, 2017, **12**, 1111-1119.
5 D. S. Choi, H. Lee, F. Tieves, Y. W. Lee, E. J. Son, W. Zhang, B. Shin, F. Hollmann and C. B. Park, *ACS Catal.*, 2019, **9**, 10562-10566.
6 J. Sun, Y. Yu, A. E. Curtze, X. Liang and Y. Wu, *Chem. Sci.*, 2019, **10**, 5519-5527.
7 J. Sun and Y. Wu, *Angew. Chem. Int. Ed.*, 2020, DOI: 10.1002/anie.202003745, Accepted Article.
8 S. Y. Choi, S. Kim, K. J. Lee, J. Y. Kim, D. S. Han and H. Park, *Appl. Catal. B*, 2019, **252**, 55-61.
9 T. H. Jeon, H. Kim, H.-i. Kim and W. Choi, *Energy Environ. Sci.*, 2020, **13**, 1730-1742.