

Supporting information

Adopting Back Reduction Current as an Additional Output Signal for Achieving Photoelectrochemical Differentiated Detection

Daye Seo,^{†, †} Sunghwan Won,^{†, †} Ji Tae Kim,[†] and Taek Dong Chung^{*, ‡, †}

[†] Department of Chemistry, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea.

[‡] Advanced Institute of Convergence Technology, Suwon-si, Gyeonggi-do 16229, Korea.

[†] These authors contributed equally to this work.

* To whom correspondence should be addressed:

tdchung@snu.ac.kr (T. D. C.) Tel.: +82-2-880-4362. Fax: +82-2-887-4354.

Table of contents:

Figure S1 and S2. Physical characterization of hematite photoanodes (S-2)

Figure S3. E_{fb} measurement of the hematite photoanode in different supporting electrolyte (S-3)

Scheme S1. Schematic illustration of two pathways of back reduction (S-4)

Figure S4 and S5. Anodic deposition of PPO and blocking the pinholes (S-5, S-6)

Figure S6. Cathodic LSV of 500 mM $[\text{Fe}(\text{CN})_6]^{3-}$ under dark condition, with a PPO-deposited hematite electrode (S-7)

Figure S7 and S8. Effect of stirring and applied potential (S-8, S-9)

Figure S9 and S10. Effect of other anions: chloride, sulfate, and borate (S-10, S-11)

Figure S11 and S12. Synthetic procedure of the Os(II) complex and its characterizations (S-12, S-13)

Figure S13. E_{fb} measurement of the pDK coated hematite photoanode (S-14)

Figure S14. CVs of catecholamines at the hematite photoanode (S-15)

Table S1. Quantitative analysis of DA, EP, and NE (S-16)

Figure S15. Transient photocurrents of low concentration of DA (S-16)

Scheme S2 and Figure S16. Reaction mechanism of catecholamines and their CVs (S-17)

Reference (S-18)

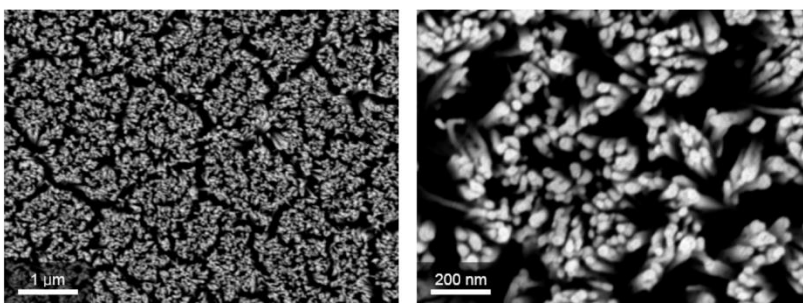


Figure S1. SEM images of a hematite electrode with different magnification.

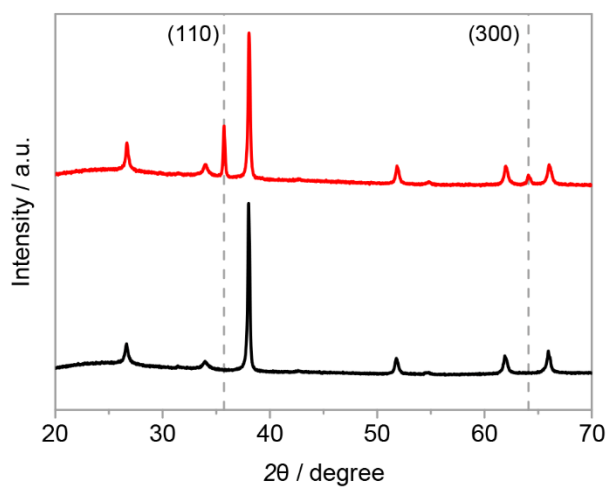


Figure S2. XRD spectra of a bare FTO substrate (black) and a hematite electrode (red). The diffraction peaks corresponding to (110) and (300) faces were observed.

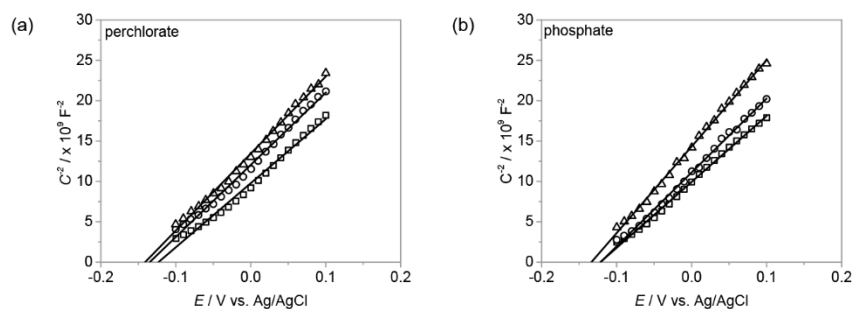
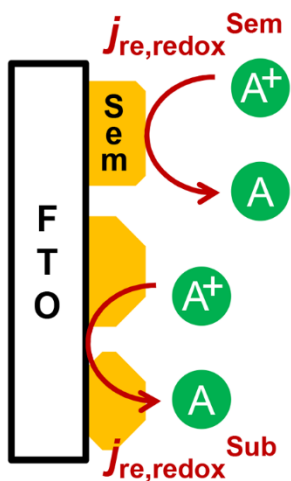


Figure S3. Representative Mott-Schottky plots for hematite obtained in (a) 0.1 M phosphate buffer solution and (b) 0.1 M perchlorate solution in the dark (square: 500 Hz, circle: 1000 Hz, triangle: 1500 Hz). E_{fb} calculated by Mott-Schottky equation ($\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} \left(E - E_{fb} - \frac{k_B T}{e} \right)$, where C is the capacitance, e is the electron charge, ϵ is the dielectric constant of hematite (80)¹, ϵ_0 is the permittivity of vacuum, N_D is the carrier density, E is the applied potential, and $k_B T/e$ is a temperature-dependent correction term.) was -0.151 V and -0.150 V in perchlorate and phosphate solution respectively. E_{fb} 's measured at three different hematite electrodes were averaged.



Scheme S1. Schematic illustration of two pathways of back reduction. Back reduction of photooxidized species (A^+) can occur at the semiconductor electrode ($j_{\text{re,redox}}^{\text{Sem}}$) and at the conductive substrate ($j_{\text{re,redox}}^{\text{Sub}}$) exposed through the pinholes of semiconductor. Therefore, $j_{\text{re,redox}}$ is the sum of $j_{\text{re,redox}}^{\text{Sem}}$ and $j_{\text{re,redox}}^{\text{Sub}}$.

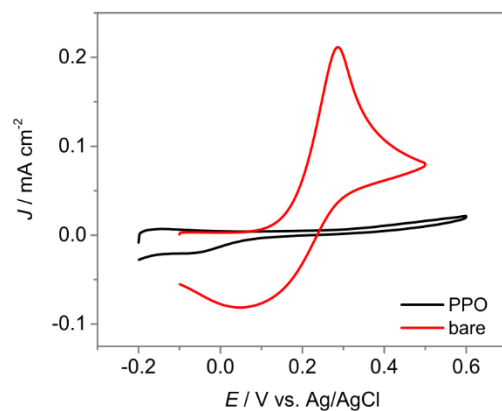


Figure S4. CVs of 1 mM $[\text{Fe}(\text{CN})_6]^{4-}$ in 0.1 M perchlorate solution (pH 6) at bare hematite (red) and PPO-deposited hematite (black) in the dark. Since no anodic current can flow through *n*-type semiconductor in the dark, PPO was oxidatively electrodeposited onto the electrode in the dark so that the exposed FTO surface was selectively insulated. The disappearance of the oxidation current of $[\text{Fe}(\text{CN})_6]^{4-}$ confirmed that the PPO layer effectively blocked the pinholes. The only possible electron transfer pathway of PPO-deposited hematite is through the hematite electrode.

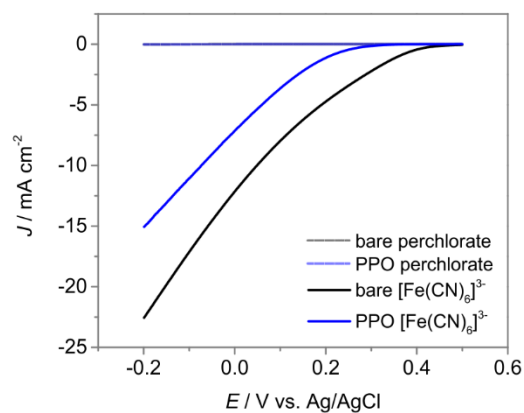


Figure S5. Cathodic LSV of 500 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M perchlorate solution (pH 6) in the dark, with (blue) or without (black) surface modification with PPO. Only FTO participated in the reduction above 0.3 V, and both hematite and FTO can reduce $[\text{Fe}(\text{CN})_6]^{3-}$ below 0.3 V even though the contribution of each pathway is not easy to quantify. Considerable portion of back reduction undergoes through the FTO, and the reaction at the conductive underlayer must affect the apparent rate constant.

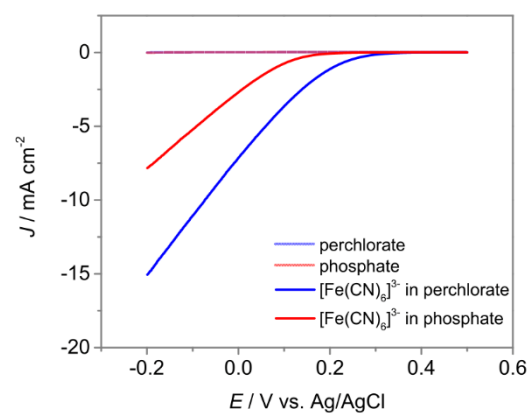


Figure S6. Cathodic LSV of 500 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M phosphate (red) and perchlorate (blue) solution (pH 6) in the dark at a PPO-deposited hematite electrode.

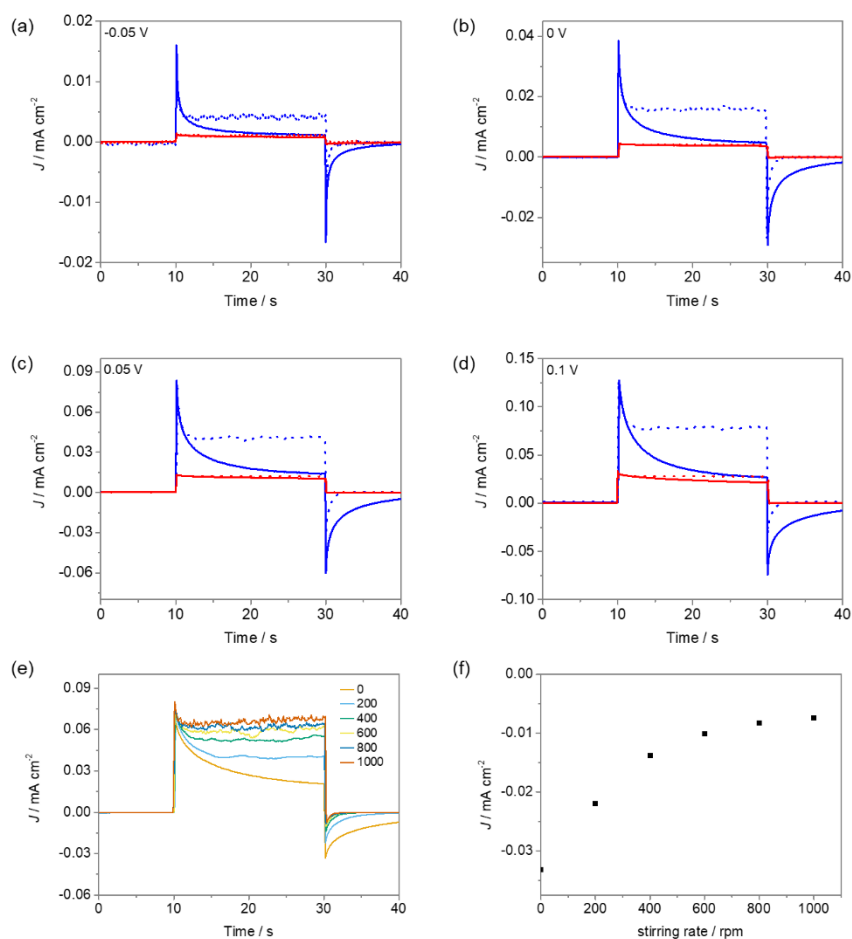


Figure S7. Transient photocurrents at various applied potential in contact with 1 mM $[\text{Fe}(\text{CN})_6]^{4-}$ solution containing 0.1 M perchlorate (blue) and 0.1 M phosphate (red), with stirring (dotted lines) and without stirring (solid lines). The stirring rate was 800 rpm. The experiments were conducted under back illumination. (a) -0.05 V, (b) 0 V, (c) 0.05 V, and (d) 0.1 V. Over all potential ranges, photocurrents in perchlorate solution were higher than those in phosphate solution. In particular, the $j_{\text{ph,steady}}$ was always significantly higher when the solution was stirred, which means that $k_{\text{ph,redox}}$ is higher with perchlorate regardless of the applied potential. (e) Transient photocurrents at 0.05 V in contact with 1 mM $[\text{Fe}(\text{CN})_6]^{4-}$ solution containing 0.1 M perchlorate with varied stirring rate. (f) $j_{\text{re,max}}$ extracted from (e) as a function of the stirring rate. $j_{\text{re,max}}$ converges after 800 rpm therefore it is inferred that the stirring rate of 800 rpm was fast enough to reduce the mass transport effect.

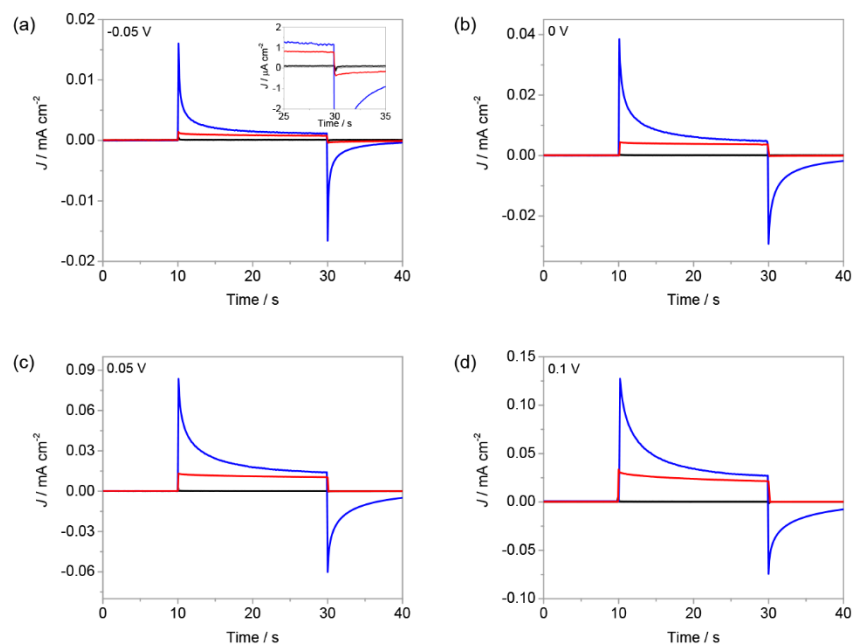


Figure S8. Transient photocurrents at various applied potential. 1 mM $[\text{Fe}(\text{CN})_6]^{4-}$ in perchlorate (blue), 1 mM $[\text{Fe}(\text{CN})_6]^{4-}$ in phosphate (red), perchlorate without $[\text{Fe}(\text{CN})_6]^{4-}$ (grey), and phosphate without $[\text{Fe}(\text{CN})_6]^{4-}$ (black). (a) -0.05 V, (b) 0 V, (c) 0.05 V, and (d) 0.1 V. The experiments were conducted under back illumination. Transient photocurrents at perchlorate without $[\text{Fe}(\text{CN})_6]^{4-}$ is almost same as those at phosphate without $[\text{Fe}(\text{CN})_6]^{4-}$ so that they are not apparently shown in the graph. Inset in (a) is a zoom in of cathodic transient current.

Over all potential ranges, both photocurrent and back reduction current with perchlorate were higher when those with phosphate even though the degree of difference was dependent on the applied potential. When the applied potential was as negative as -0.05 V, the rate of back reduction was high enough that the cathodic transient current originated from back reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ was not negligible even under phosphate condition. This result indicates that applied potential is another important factor that determines whether the back reduction occurs or not.

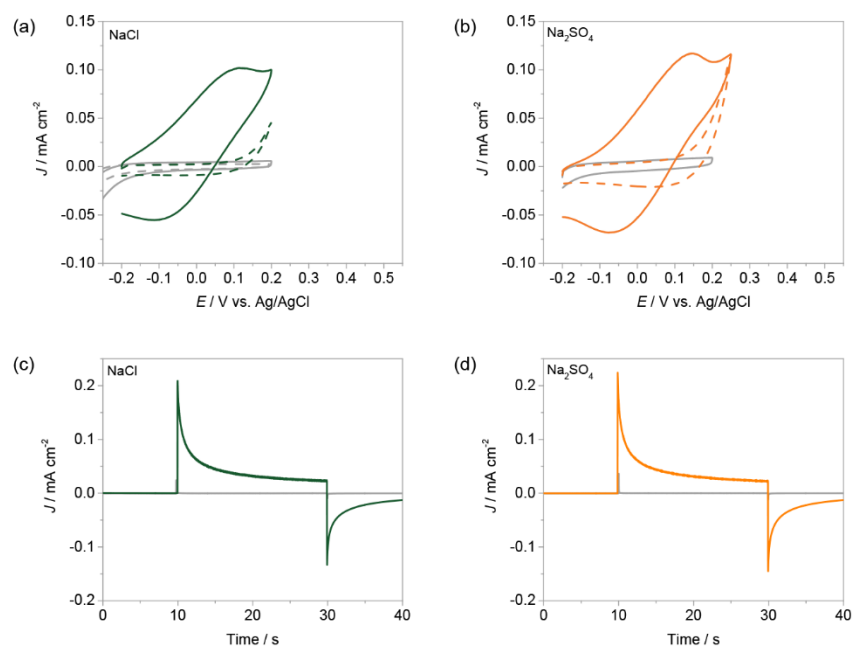


Figure S9. CVs under 1 sun illumination and transient photocurrents ($E=0.05$ V) in contact with 1 mM $[\text{Fe(CN)}_6]^{4-}$ solution containing (a, c) 0.1 M NaCl and (b, d) 0.1 M Na_2SO_4 . pH's of the solutions were adjusted to 6.0. Colored solid lines and grey solid lines show CVs and transient photocurrent with and without $[\text{Fe(CN)}_6]^{4-}$ respectively. Dotted lines in (a) and (b) show CVs in the dark.

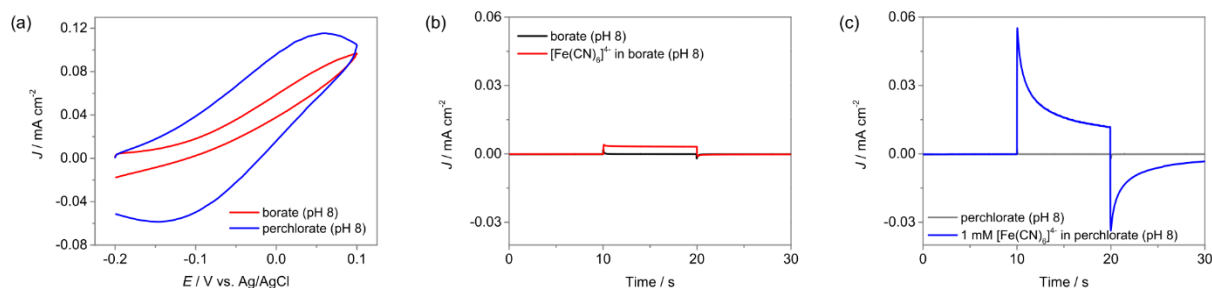


Figure S10. (a) CVs under 1sun illumination and (b, c) transient photocurrents at -0.05 V in contact with $1 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}$ solution containing 0.1 M borate (red) and perchlorate (blue). Black and grey lines in (b) and (c) are transient photocurrents without $[\text{Fe}(\text{CN})_6]^{4-}$. pH of the solution was buffered or adjusted to 8. No noticeable difference in transient photocurrent was observed between pH 6 and 8 in the presence of perchlorate (Figure 1c and Figure S7c), even though the hematite has slightly different intrinsic surface charge in two cases.

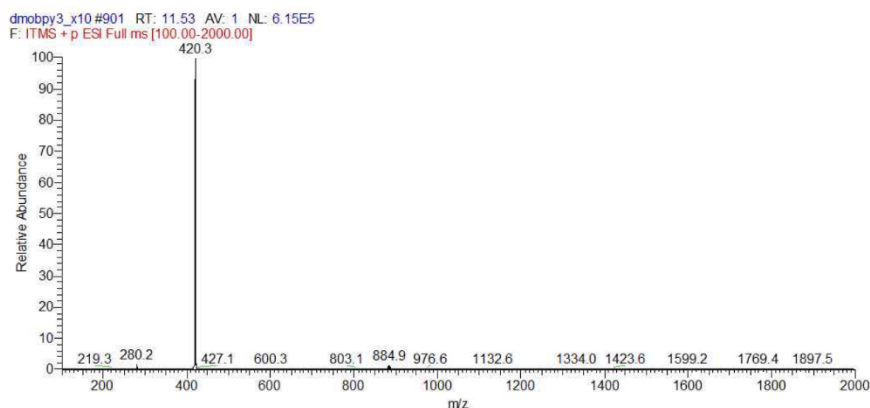


Figure S11. Mass spectrum of $[\text{Os}(\text{dmo-bpy})_3]\text{Cl}_2$. Procedure for Os complex synthesis is described below.

Materials. 4,4'-dimethoxy-2,2'-bipyridine, potassium hexachloroosmate(IV), and ammonium hexafluorophosphate were purchased from Sigma-Aldrich. Methanol, dimethylformamide were purchased from Daejung Chemicals. All chemicals were used without further purification. Ultrapure deionized water (resistivity $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) used in this study was produced with a Barnstead NANO pure water system.

Procedure. $[\text{Os}(\text{dmo-bpy})_3]\text{Cl}_2$ was synthesized according to the reported procedure.² 100 mg of K_2OsCl_6 and 145 mg of 4,4'-dimethoxy-2,2'-bipyridine (dmo-bpy) were dissolved in a mixture of 5 mL water + 5 mL methanol + 5 mL dimethylformamide. The solution was refluxed for 60 h under nitrogen atmosphere. The mixture was cooled to room temperature and the solvent was removed in vacuo. Then, the product was precipitated by addition of an aqueous solution of ammonium hexafluorophosphate, and isolated by filtration. The precipitate was purified by column chromatography, and the counter anion was exchanged to chloride by anion exchange chromatography.

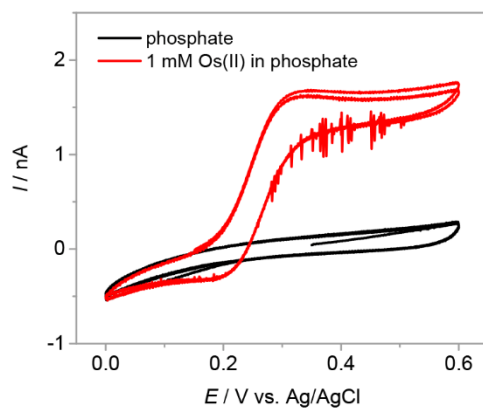


Figure S12. CVs at platinum ultramicroelectrode ($d = 25 \mu\text{m}$) in 0.1 M phosphate solution (pH 6) in the absence (black) and presence (red) of 1 mM Os complex. The solution was purged with nitrogen gas. Significant anodic current and negligible cathodic current indicate that the Os complex is mainly composed of reduced form rather than oxidized form.

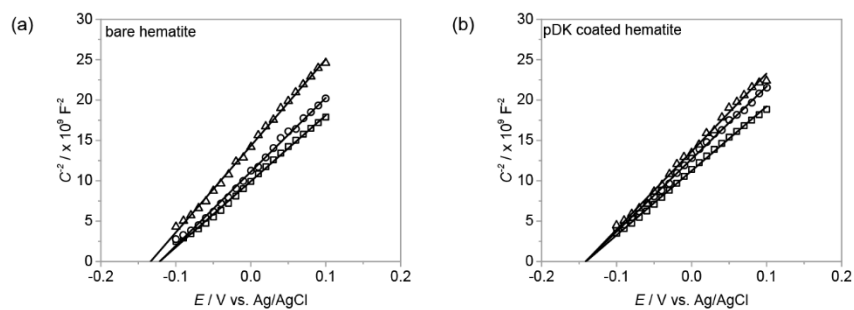


Figure S13. Representative Mott-Schottky plots for (a) bare hematite and (b) pDK coated hematite obtained in 0.1 M phosphate buffer solution in the dark (square: 500 Hz, circle: 1000 Hz, triangle: 1500 Hz). E_{fb} 's calculated by the equation used in Figure S3 were -0.150 V and -0.168 V for bare and pDK coated hematite respectively. E_{fb} 's measured at three different hematite electrodes averaged.

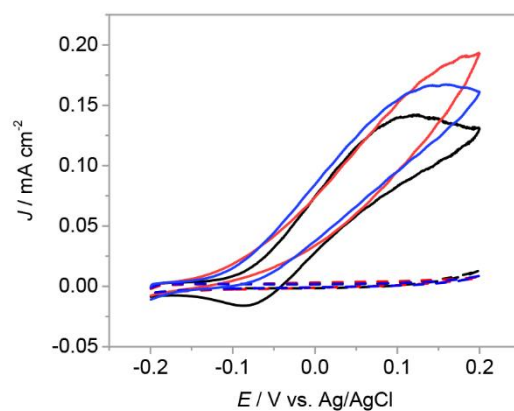


Figure S14. CVs at hematite photoanode in 0.1 M pH 7.4 phosphate solution in the presence of 500 μM DA (black), EP (red) and NE (blue). Solid lines are CVs under 1sun illumination and dotted lines are CVs in the dark. Photocurrents of the three different molecules are featureless in terms of the shape and magnitude.

Table S1. Quantitative analysis of DA, EP, and NE using anodic steady-state current and cathodic transient current. All the figures are come from the calibration curves in Figure 3 and 4. LODs are defined as the lowest concentration whose signal is above the three-time standard deviation of the background signal.

	DA		EP	NE	
	Anodic	Cathodic	Anodic	Anodic	Cathodic
Slope (mA/ μ M)	2.32×10^{-5}	3.50×10^{-5}	4.44×10^{-5}	4.56×10^{-5}	1.99×10^{-5}
y-intercept (μ M)	6.07×10^{-4}	1.18×10^{-3}	6.54×10^{-4}	9.62×10^{-4}	6.35×10^{-4}
R ²	0.991	0.984	0.996	0.993	0.984
LOD (μ M)	12.4	10.3	6.47	6.31	18.1

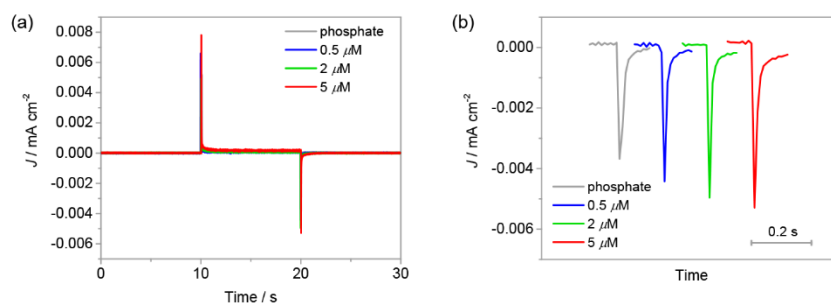
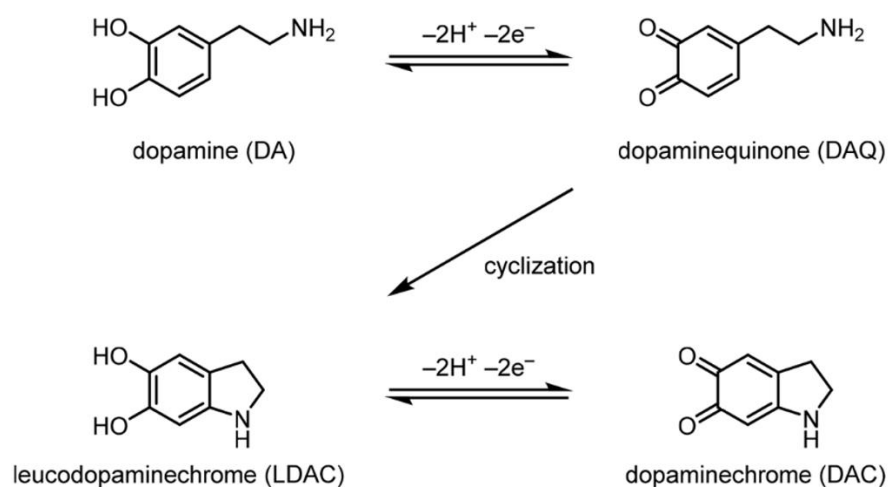


Figure S15. (a) Transient photocurrents of low concentration of DA (0, 0.5, 2, and 5 μ M) in 0.1 M pH 7.4 phosphate solution. (b) is a zoom in of cathodic transient current in (a) and the x-axis (time) was adjusted to clarify the trend of the magnitude.



Scheme S2. The *ECE* mechanism of DA electrochemistry. EP and NE have the same *ECE* reaction mechanism, but the rates of the chemical reaction (cyclization) are different from each other.

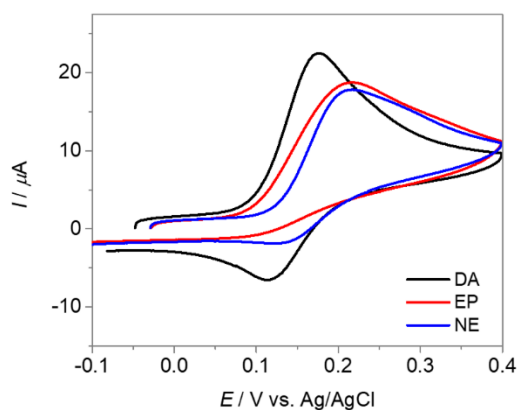


Figure S16. CVs at glassy carbon electrode in 0.1 M pH 7.4 phosphate solution in the presence of 500 μM DA (black), EP (red) and NE (blue). The magnitude of the cathodic peak current reflects the rate of the chemical reaction (cyclization) following the first two electron transfer oxidation.

References

- [1] Cesar, I.; Sivula, K.; Kay, A.; Zboril, R.; Grätzel, M. *J. Phys. Chem. C* **2009**, *113*, 772–782.
- [2] Zakeeruddin, S. M.; Fraser, D. M.; Nazeeruddin, M. –K.; Grätzel, M. *J. Electroanal. Chem.* **1992**, *337*, 253–283.