Supporting Information

Electrochemical Production of Hydrogen Coupled with the Oxidation of Arsenite

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Total 9 pages

Tables S1-S2 and Figures S1-S6

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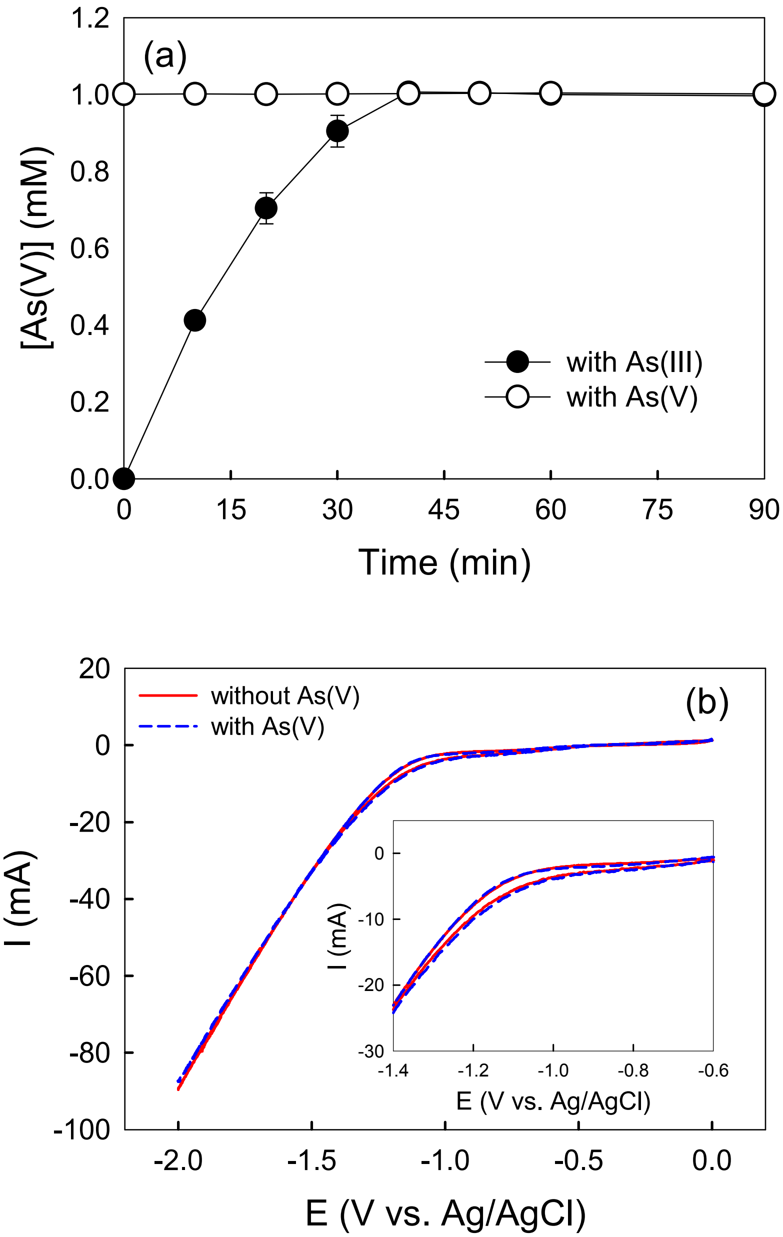

Figure S1. (a) Generation of As(V) from the oxidation of As(III) (in the presence of As (III)) and decrease of As(V) from the reduction of As(V) (in the presence of As(V)). (b) Cyclic voltammograms in the absence and presence of As(V). Experimental conditions: E_{cell} = 3.0 V (for a), [NaCl] = 50 mM, [As(III)] or [As(V)] = 1 mM, and continuously Ar-purged.

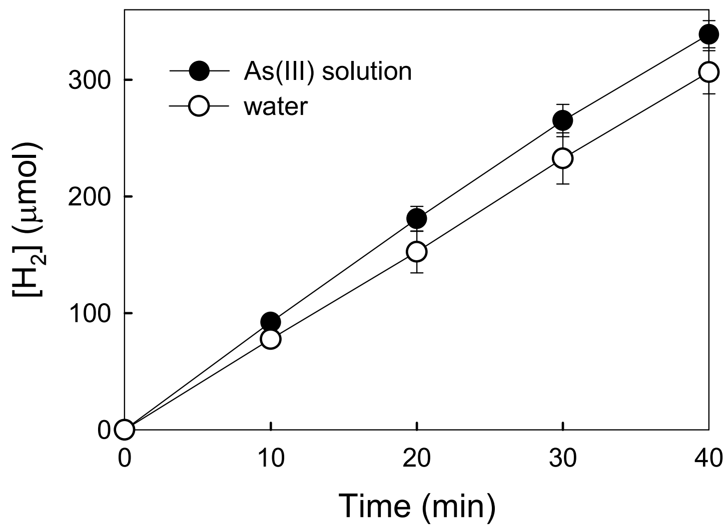

Figure S2. Time profiles of H_2 production in the As(III) solution and the water. Experimental conditions: E_{cell} = 3.0 V, [NaCl] = 50 mM, and [As(III)] = 1 mM.

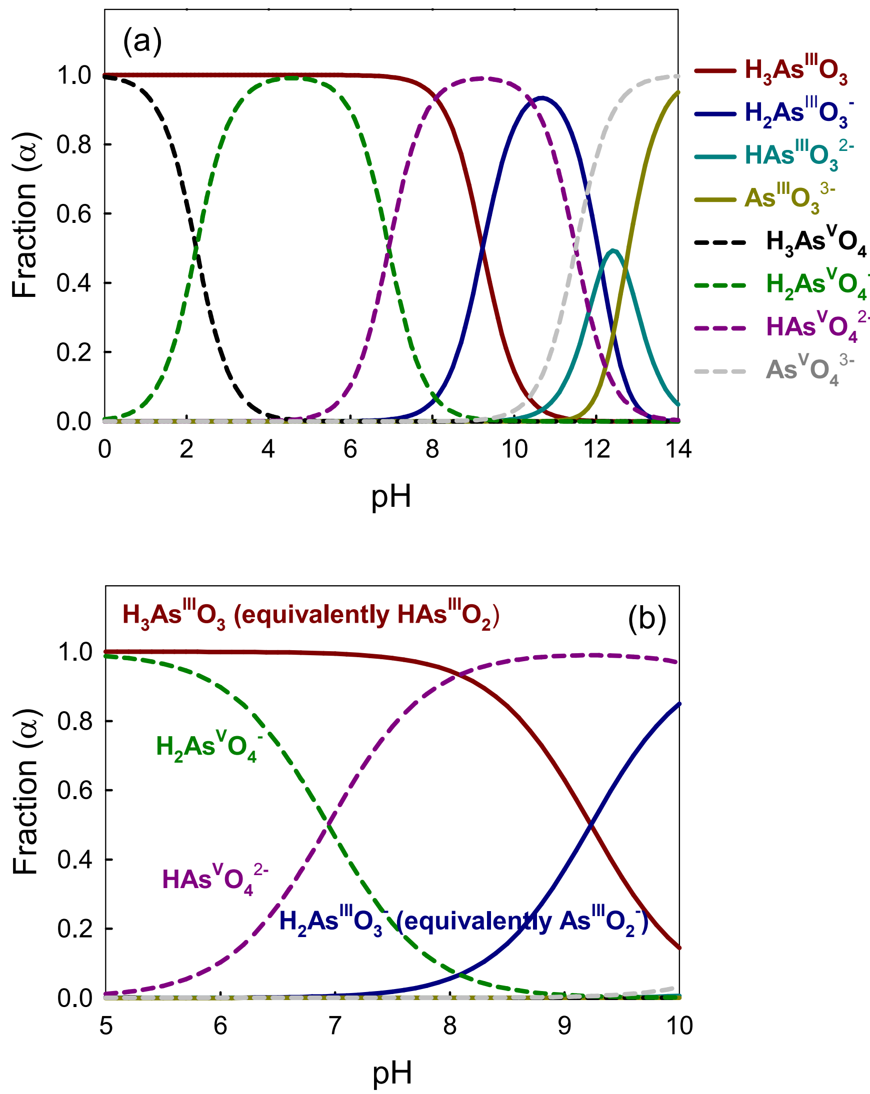

Figure S3. Speciation of As(III) and As(V) as a function of pH in the range of (a) 0 – 14 and (b) 5 – 10. The stepwise acid dissociation constants (pK_a) of arsenite and arsenate were obtained from ref. 1. As(III): $pK_{a1} = 9.23$, $pK_{a2} = 12.13$, and $pK_{a3} = 12.71$; As(V): $pK_{a1} = 2.24$, $pK_{a2} = 6.94$, and $pK_{a3} = 11.50$.

Based on Figure S3, the three reactions below (eqs S1 – S3) are mainly took place in the pH range of 5 – 10.

$$HAs^{III}O_2 \rightarrow H_2As^{V}O_4^{-} \quad \text{(S1)}$$
$$HAs^{III}O_2 \rightarrow HAs^{V}O_4^{2-} \quad \text{(S2)}$$
$$As^{III}O_2^{-} \rightarrow HAs^{V}O_4^{2-} \quad \text{(S3)}$$

Table S1. Standard Reduction Potential (E^0) of Elementary Reactions

Reaction	E^0 (V_{NHE})	Ref.
$H_2As^VO_4^- + 3H^+ + 2e^- \rightarrow HAs^{III}O_2 + 2H_2O$	0.67	2
$HAs^VO_4^{2-} + 4H^+ + 2e^- \rightarrow HAs^{III}O_2 + 2H_2O$	0.88	2
$HAs^VO_4^{2-} + 3H^+ + 2e^- \rightarrow As^{III}O_2^- + 2H_2O$	0.61	2
$Cl\bullet + e^- \rightarrow Cl^-$	2.4	3
$Cl_2\bullet^- + e^- \rightarrow 2Cl^-$	2.0	3
$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49	3
$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90	3
$O_2 + e^- \rightarrow O_2\bullet^-$	−0.33	4
$O_2\bullet^- + e^- + H^+ \rightarrow HO_2^-$	1.00	4
$O_2\bullet^- + e^- + 2H^+ \rightarrow H_2O_2$	1.71	4

Table S2. Reactions Among Reactive Chlorine Species, As(III), and $O_2{\bullet}^-$

(Unit: V_{NHE})

Entry	Reaction	E^0	E^0@pH=5[a]	E^0@pH=7.5[a]	E^0@pH=10[a]
Reactions between As(III) and reactive chlorine species					
A-1	$As^{III}O_2^- + x Cl{\bullet} + (2-x)Cl_2{\bullet}^- + 2H_2O \rightarrow HAs^{V}O_4^{2-} + (4-x)Cl^- + 3H^+$				
A-2	$HAs^{III}O_2 + x Cl{\bullet} + (2-x)Cl_2{\bullet}^- + 2H_2O \rightarrow HAs^{V}O_4^{2-} + (4-x)Cl^- + 4H^+$				
A-3	$HAs^{III}O_2 + x Cl{\bullet} + (2-x)Cl_2{\bullet}^- + 2H_2O \rightarrow H_2As^{V}O_4^- + (4-x)Cl^- + 3H^+$				
A-4	$As^{III}O_2^- + HOCl$ (or OCl^-) $+ H_2O \rightarrow HAs^{V}O_4^{2-} + Cl^- + 2H^+$ (or H^+)				
A-5	$HAs^{III}O_2 + HOCl$ (or OCl^-) $+ H_2O \rightarrow HAs^{V}O_4^{2-} + Cl^- + 3H^+$ (or $2H^+$)				
A-6	$HAs^{III}O_2 + HOCl$ (or OCl^-) $+ H_2O \rightarrow H_2As^{V}O_4^- + Cl^- + 2H^+$ (or H^+)				
Reactions between As(III) and $O_2{\bullet}^-$					
B-1	$As^{III}O_2^- + 2O_2{\bullet}^- + 2H_2O \rightarrow HAs^{V}O_4^{2-} + 2HO_2^- + H^+$	0.39	NA[b]	NA	0.69
B-2	$As^{III}O_2^- + 2O_2{\bullet}^- + 2H_2O + H^+ \rightarrow HAs^{V}O_4^{2-} + 2H_2O_2$	1.10	NA	NA	0.81
B-3	$HAs^{III}O_2 + 2O_2{\bullet}^- + 2H_2O \rightarrow HAs^{V}O_4^{2-} + 2HO_2^- + 2H^+$	0.12	NA	0.56	0.71
B-4	$HAs^{III}O_2 + 2O_2{\bullet}^- + 2H_2O \rightarrow HAs^{V}O_4^{2-} + 2H_2O_2$	0.83	NA	0.83	0.83
B-5	$HAs^{III}O_2 + 2O_2{\bullet}^- + 2H_2O \rightarrow H_2As^{V}O_4^- + 2HO_2^- + H^+$	0.33	0.48	0.55	NA
B-6	$HAs^{III}O_2 + 2O_2{\bullet}^- + 2H_2O + H^+ \rightarrow H_2As^{V}O_4^- + 2H_2O_2$	1.04	0.89	0.82	NA
Reactions between reactive chlorine species and $O_2{\bullet}^-$					
C-1	$O_2{\bullet}^- + Cl{\bullet} \rightarrow O_2 + Cl^-$	2.73	2.73	2.73	2.73
C-2	$O_2{\bullet}^- + Cl_2{\bullet}^- \rightarrow O_2 + 2Cl^-$	2.33	2.33	2.33	2.33
C-3	$2O_2{\bullet}^- + HOCl + H^+ \rightarrow 2O_2 + Cl^- + H_2O$	1.82	1.67	1.60	NA
C-4	$2O_2{\bullet}^- + OCl^- + H_2O \rightarrow 2O_2 + Cl^- + 2OH^-$	1.23	NA	1.61	1.47

[a] E^0 was obtained from the Nernst equation of each reaction (see table S1 for the elementary reactions of each reaction and their E^0). [b] NA = not available.

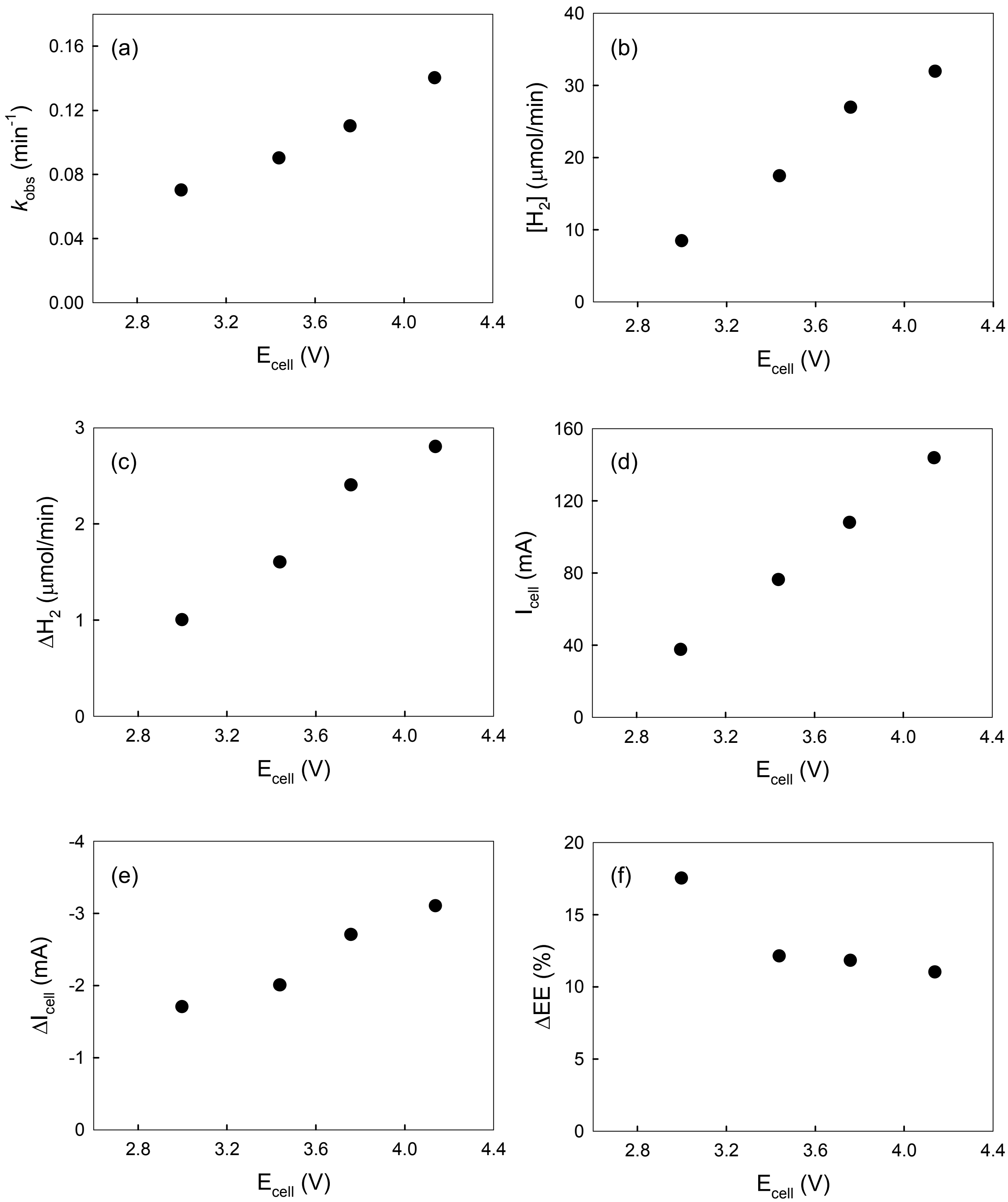

Figure S4. Relationship between E_{cell} and (a) k_{obs}, (b) H_2 production, (c) ΔH_2, (d) I_{cell}, (e) ΔI_{cell}, and (f) ΔEE.

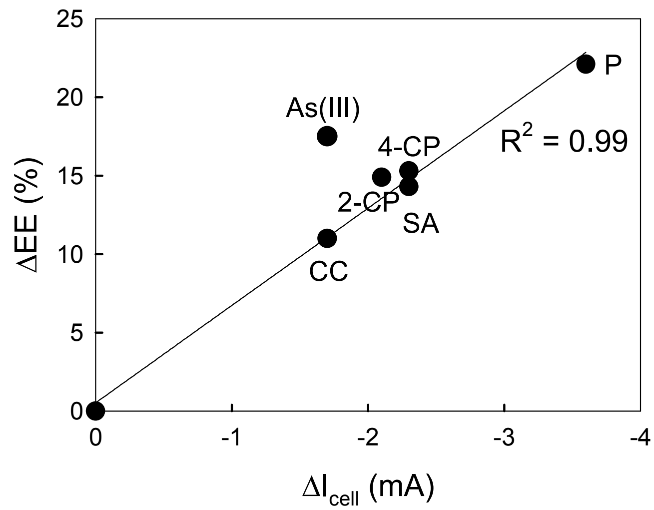

Figure S5. Relationship between ΔI_{cell} and ΔEE depending on the kind of substrate.

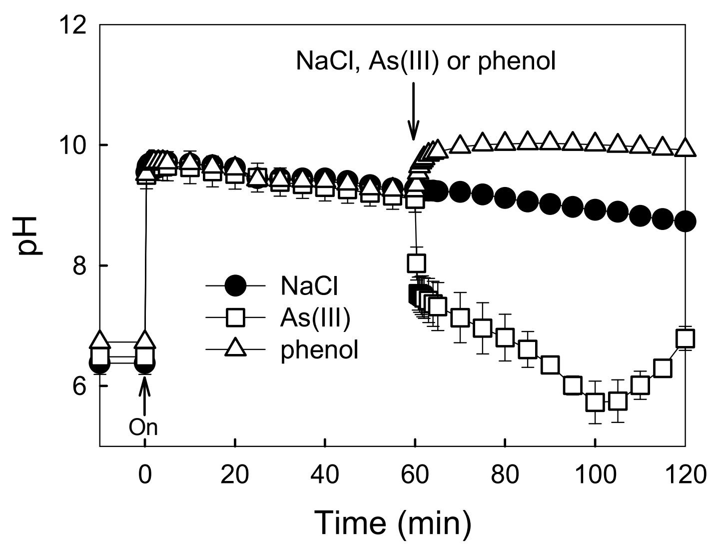

Figure S6. Time profiles of pH change by the addition of NaCl (electrolyte), As(III), and phenol. Experimental conditions: E_{cell} = 3.0 V, [NaCl] = 50 mM, and continuously Ar-purged. NaCl, As(III) or phenol (1 mM) was added to the electrolyte (as indicated by arrow) in the course of electrolysis. The pHs of substrate stock solution were 4.4 (for phenol), 6.5 (for NaCl), and 10.2 (for As(III)), respectively. Therefore, the pH change by the addition of substrate is not due to the pH difference between electrolyte and substrate stock solution.

References

1. Sadiq, M.; Zaidi, T. H.; Mian, A. A. Environmental behavior of arsenic in soils: theoretical. *Water, Air, Soil Pollut.* **1983**, *20*, 369-377.
2. Bard, A. J., Parsons, R., Jordan, J., Eds.; *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.
3. Park, H.; Vecitis, C. D.; Hoffmann, M. R. Electrochemical water splitting coupled with organic compound oxidation: the role of active chlorine species. *J. Phys. Chem. C* **2009**, *113*, 7935-7945.
4. Wardman, P. Reduction potentials of one-electron couples involving free radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637-1755.