Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

An overall water-splitting polyoxometalate catalyst for the electromicrobial conversion of CO_2 in neutral water

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Figure S1. Energy-dispersive X-ray spectrum (EDS) combined with SEM images.

Figure S2. (a) Cu 2p, (b) Co 2p, (c) P 2p and (d) W 4f XPS spectra of as-prepared Cu_6Co_7/CC powder and Cu_6Co_7/CC film.

Figure S3. I-t curves for HER and H_2 evolving.

Figure S4. I-t curves for OER.

Figure S5. Linear sweep voltammetry curves of the ORR for Cu_6Co_7/CC after HER test (black) and Pt/C/CC (red) in O_2 saturated in phosphate buffer (pH 7) at a scan rate of 10 mV/s.

Figure S6. SEM images of Cu_6Co_7/CC after HER test (a) and OER test (b).

Figure S7. (a) Cu 2p, (b) Co 2p, (c) P 2p and (d) W 4f XPS spectra of Cu_6Co_7/CC after HER and OER tests.

Figure S8. XRD spectra of Cu_6Co_7/CC after HER and OER tests.

Figure S9. SEM images of Cu_6Co_7/CC after the overall water splitting reaction ((a) anode, (b) cathode) .

Figure S10. The dependence of the growth of *R. eutropha* on hydrogen evolution during the electrolysis with CO_2 (E_{appl} =1.8 V) .

Table S1. Comparison of HER performances of different catalysts under neutral conditions.

Table S2. Comparison of the performance of Cu_6Co_7/CC to other bioelectrochemical systems for CO_2 fixation.

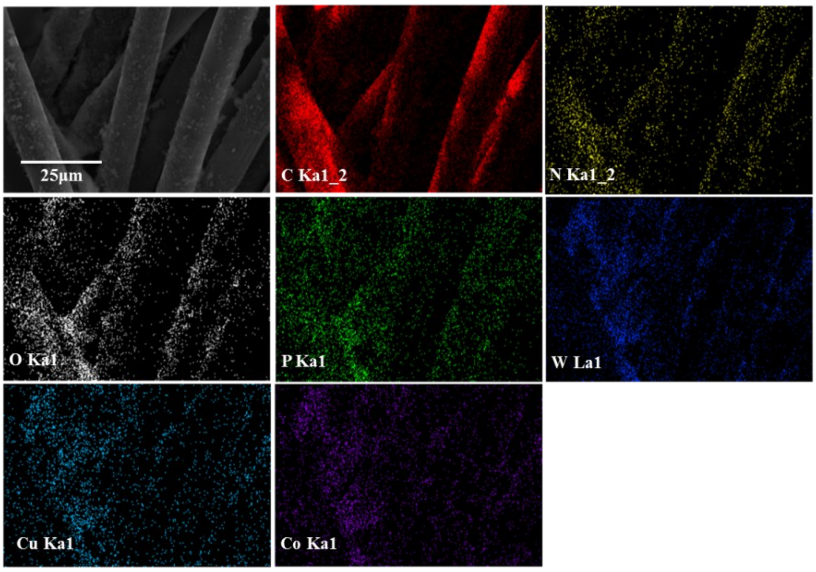
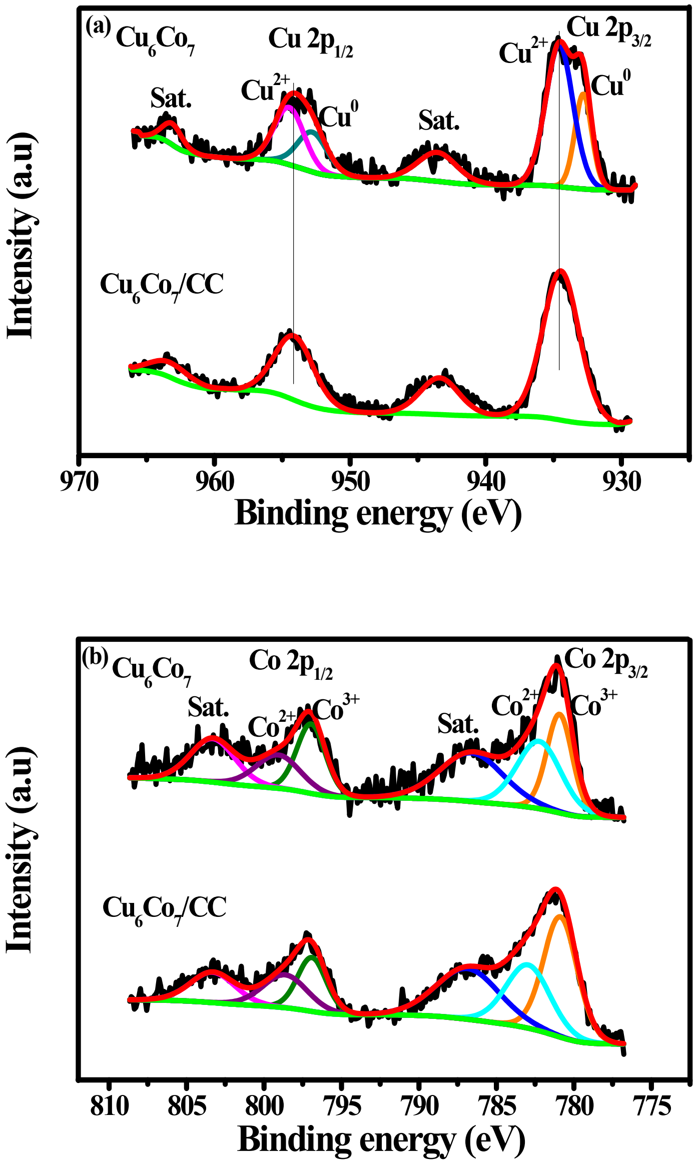
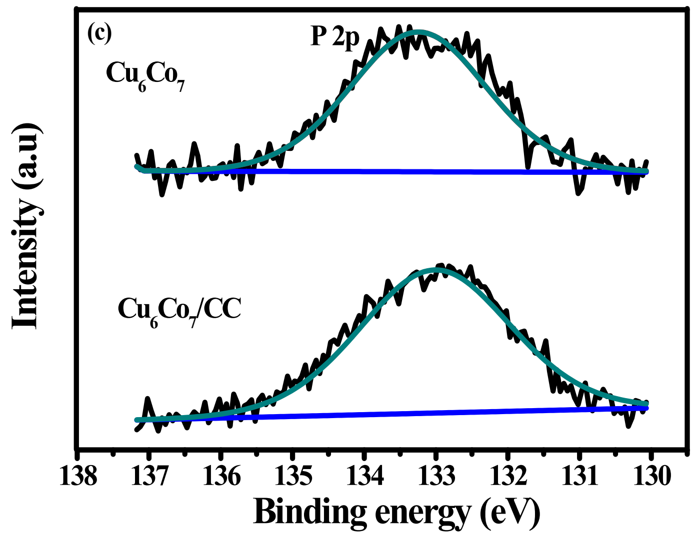


Figure S1. Energy-dispersive X-ray spectrum (EDS) combined with SEM images of the Cu_6Co_7/CC film.



(a) Cu6Co7
Cu 2p1/2
Cu 2p3/2
Sat.
Cu2+
Cu0
Sat.
Cu2+
Cu0
Cu6Co7/CC
Intensity (a.u)
970 960 950 940 930
Binding energy (eV)
(b) Cu6Co7
Co 2p1/2
Co 2p3/2
Sat.
Co2+
Co3+
Sat.
Co2+
Co3+
Cu6Co7/CC
Intensity (a.u)
810 805 800 795 790 785 780 775
Binding energy (eV)



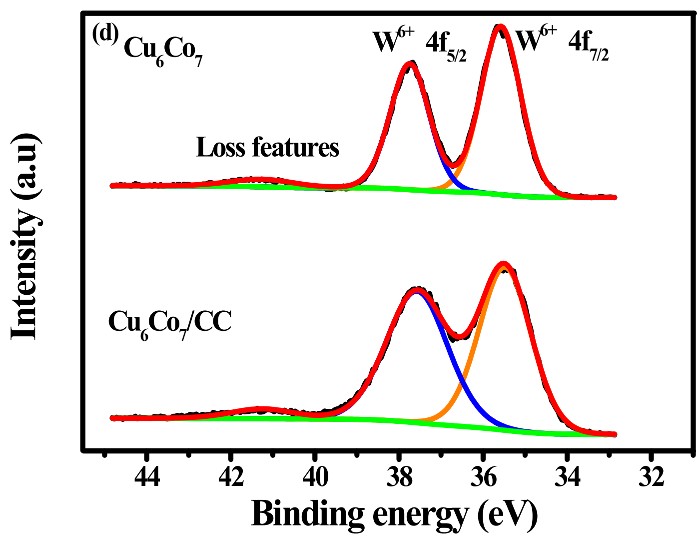


Figure S2. (a) Cu 2p, (b) Co 2p, (c) P 2p and (d) W 4f XPS spectra of as-prepared Cu_6Co_7/CC powder and Cu_6Co_7/CC film.

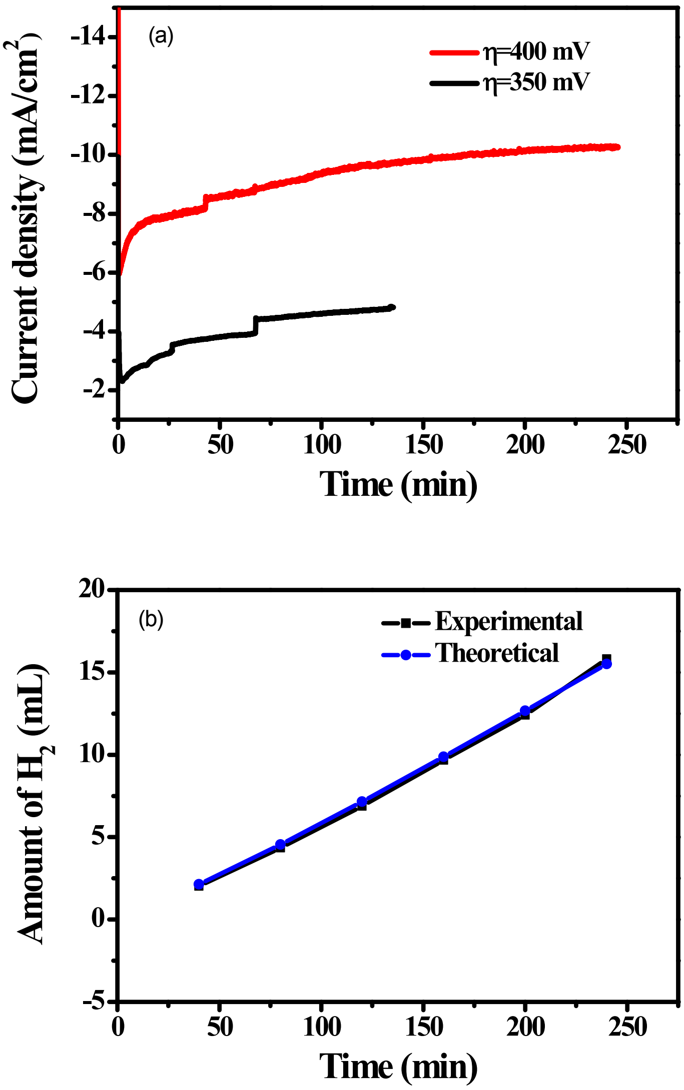


Figure S3. (a) I-t curves for Cu_6Co_7/CC at a fixed overpotential of 400 and 350 mV for HER proves, (b) The theoretically calculated and experimentally measured amount of evolved hydrogen during electrolysis process at an overpotential of 400 mV.

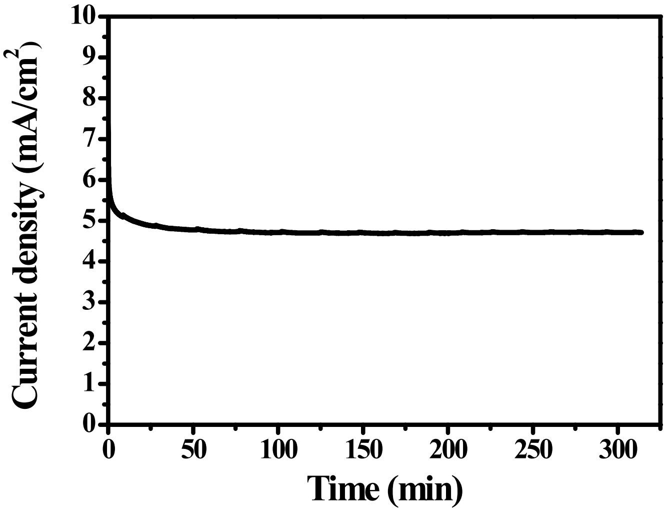
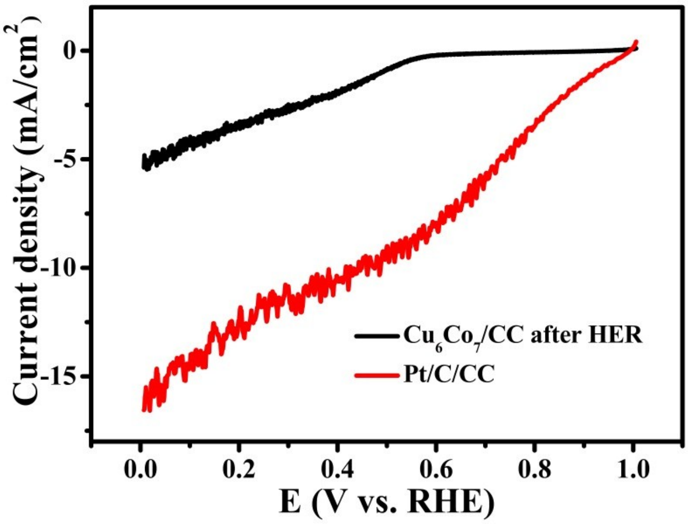


Figure S4. I-t curves for Cu_6Co_7/CC at a fixed overpotential of 400 mV for OER.



Figures S5. Linear sweep voltammetry curves of the ORR for Cu_6Co_7/CC after HER test (black) and Pt/C/CC (red) in O_2 saturated in phosphate buffer (pH 7) at a scan rate of 10 mV/s.

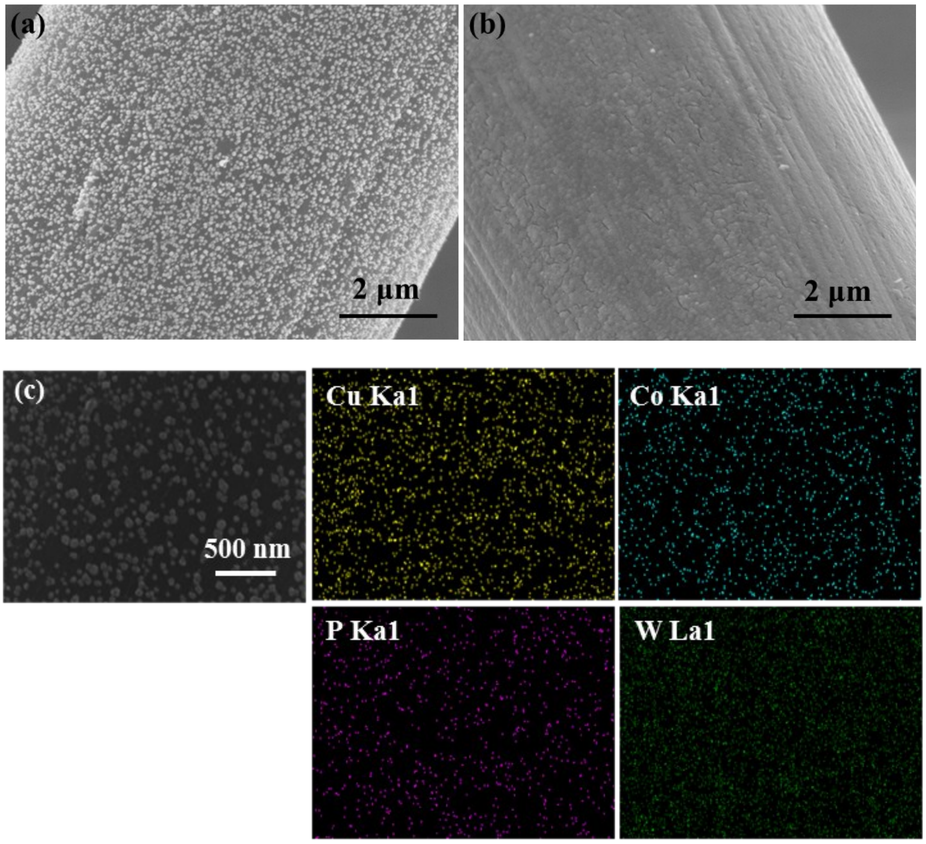
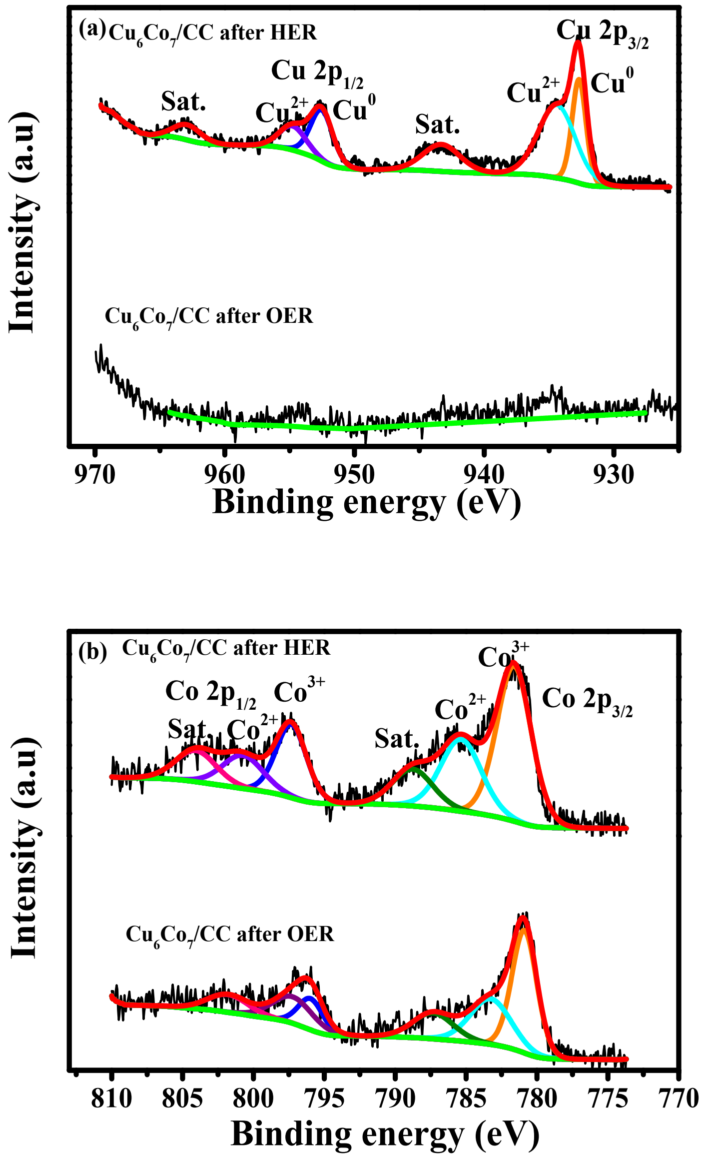


Figure S6. SEM images of Cu_6Co_7/CC after HER (a) and OER tests (b), (c) EDS combined with SEM images of the Cu_6Co_7/CC after HER test.



(a) Cu6Co7/CC after HER
Cu 2p3/2
Cu 2p1/2
Sat.
Cu2+
Cu0
Sat.
Cu2+
Cu0
Cu6Co7/CC after OER
Intensity (a.u)
970
960
950
940
930
Binding energy (eV)
(b) Cu6Co7/CC after HER
Co3+
Co 2p1/2
Co3+
Co 2p3/2
Co2+
Sat.
Co2+
Sat.
Cu6Co7/CC after OER
Intensity (a.u)
810
805
800
795
790
785
780
775
770
Binding energy (eV)

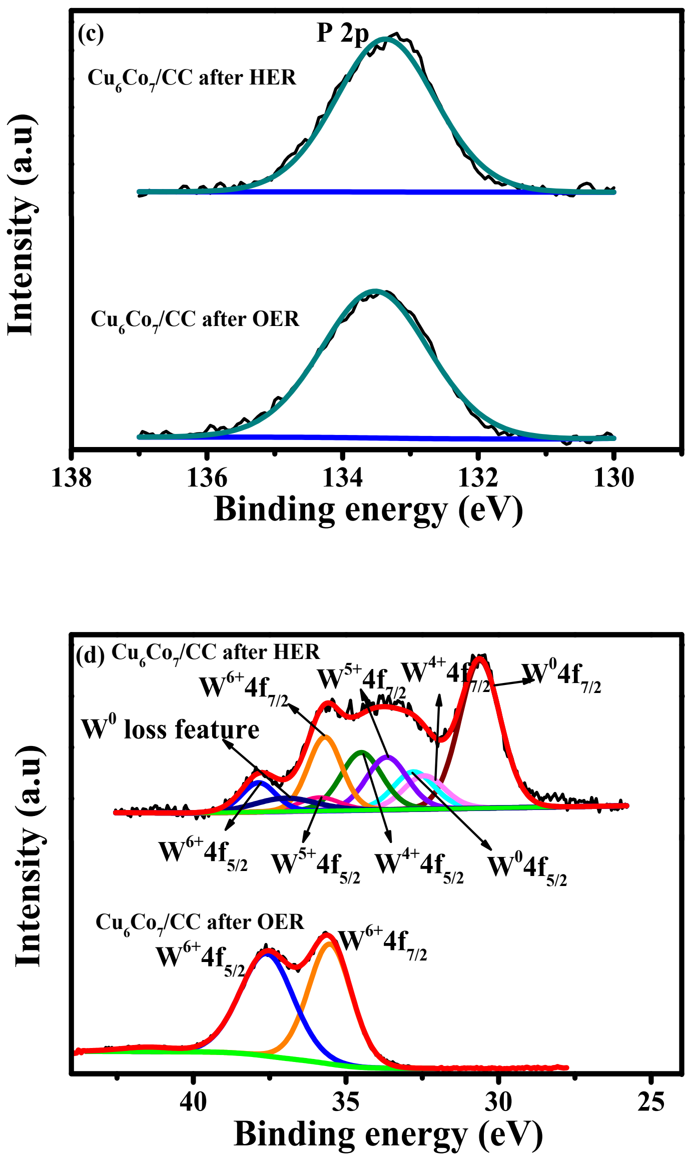


Figure S7. (a) Cu 2p, (b) Co 2p, (c) P 2p and (d) W 4f XPS spectra of Cu_6Co_7/CC after HER and OER tests.

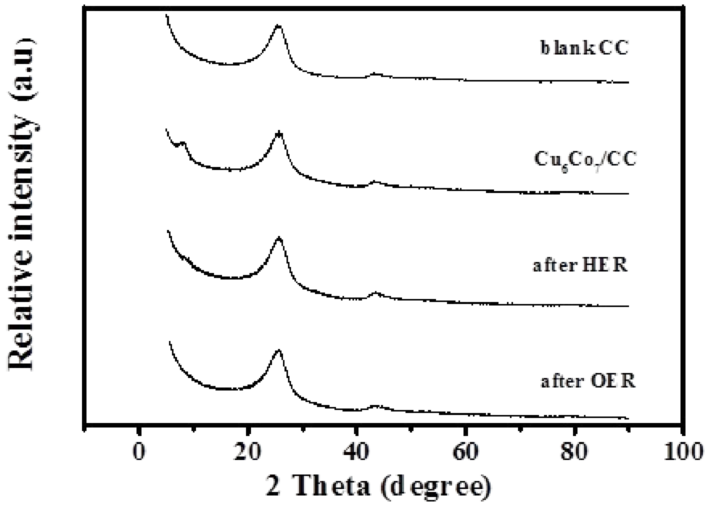


Figure S8. XRD spectra of Cu_6Co_7/CC after HER and OER tests.

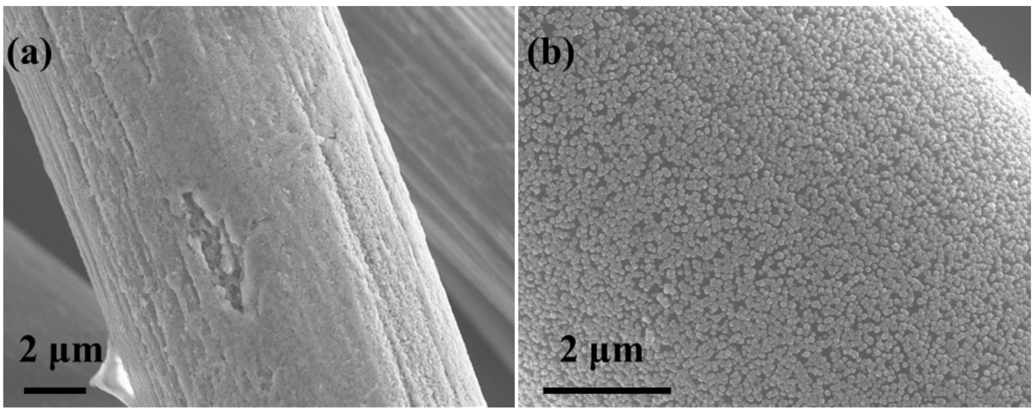


Figure S9. SEM images of Cu_6Co_7/CC after the overall water splitting reaction ((a) anode, (b) cathode) .

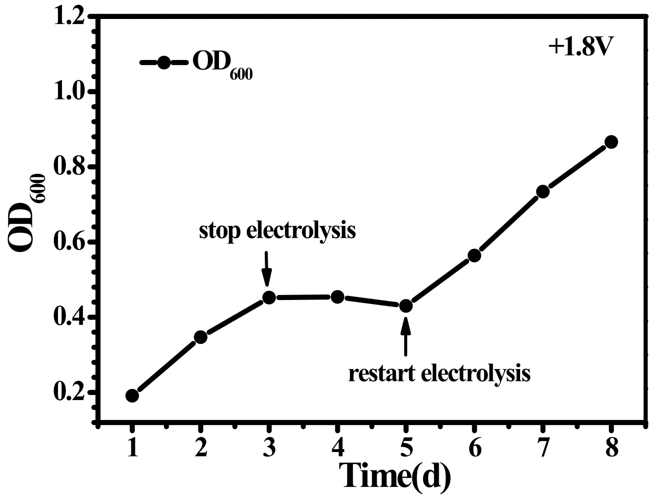


Figure S10. The dependence of the growth of *R. eutropha* on hydrogen evolution during the electrolysis with CO_2. (E_{appl} =1.8 V)

Table S1. Comparison of HER performances of different catalysts under neutral conditions.

Catalyst	Electrolyte	J^a (mA cm^{-2})	η^b (mV vs. RHE)	Tafel slope (mV dec^{-1})	Ref.
Cu_6Co_7/CC	pH 7	10	356	96	This work
		50	417		
		100	439		
H_2-CoCat	pH 7	2.0	385	140	[1]
Co(bpbH_2)Cl_2	pH 7	1.0	1148	N/A	[2]
Co-HNP	pH 7	10	85	38	[3]
		100	237		
		50	180		
Co-S	pH 7	50	397	93	[4]
Carbon-armored Co_9S_8 nanoparticle	pH 7	10	280	N/A	[5]
Cu(II) 1,2-ethylenediamine	pH 7	1.0	157	127	[6]
FeS, pyrrhotite	pH 7	0.7	450	150	[7]
Co_9S_8/CC	pH 7	10	175	N/A	[8]

		50	295		
Co-NRCNTs	pH 7	100	540	N/A	[9]

[a] Current density (mA cm^{-2})

[b] Overpotential (mV vs. RHE)

N/A These values were unavailable

References for **Table S1**:

[1] S. Cobo, J. Heidkamp, P.-A.Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Jousselme, V. Ivanova, H. Dau, S. Palacin,; M. Fontecave, V. Artero, *Nat. Mater.* **2012**, *11*, 802.

[2] Z.-Q. Wang, L.-Z. Tang, Y.-X. Zhang, S.-Z. Zhan, J.-S. Ye, *J. Power Sources* **2015**, *287*, 50.

[3] B. Liu, L. Zhang, W. Xiong, M. Ma, *Angew. Chem. Int. Ed.* **2016**, *55*, 6725.

[4] Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. R. Long, P. Yang, C. J. Chang, *J. Am. Chem. Soc.* **2013**, *135*, 17699.

[5] L.-L. Feng, G.-D. Li, Y. Liu, Y. Wu, H. Chen, Y. Wang, Y.-C. Zou, D. Wang, X. Zou, *ACS Appl. Mater. Interfaces* **2015**, *7*, 980.

[6] X. Liu, S. Cui, Z. Sun, P. Du, *Chem.Commun.* **2015**, *51*, 12954.

[7] C. Di Giovanni, W.-A. Wang, S. Nowak, J.-M. Grenèche, H. Lecoq, L. Mouton, M. Giraud, C. Tard, *ACS Catal.* **2014**, *4*, 681.

[8] L.-L. Feng, M. Fan, Y. Wu, Y. Liu, G.-D. Li, H. Chen, W. Chen, D.Wang, X. Zou, *J. Mater. Chem. A* **2016**, *4*, 6860.

[9] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa, *Angew. Chem. Int. Ed.* **2014,** *53*, 4372.

Table S2. Comparison of the performance of Cu_6Co_7/CC to other bioelectrochemical systems for CO_2 fixation.

Cathode | Anode	**Organism**	E_{appl}	**Product**	η_{elec}	η_{SCE}	**Ref.**

Cu_6Co_7/CC | Cu_6Co_7/CC	*R. eutropha* H16	1.8	Biomass	41%	7.4%	This work
		2.0		50%	9%	
		2.2		55%	9.9%	
Pt | Pt	*R. eutropha* H16	5.0	Biomass	4.8%	0.9%	[1]
CoP | CoPi	*R. eutropha* H16	2.0	Biomass	54%	9.7%	[2]
			PHB	36%	6.4%	
CoPi | SS	*R. eutropha* H16	3.0	Biomass	4.6%	0.8%	[3]
CoPi | NiMoZn	*R. eutropha* H16	2.7	Biomass	13%	2.3%	[3]
CoPi |SS	*R. eutropha* Re2133-pEG12	3.0	Biomass	4.6%	0.8%	[3]
Pt | In	*R. eutropha* LH74D	4.0	Biomass	1.8%	0.3%	[4]
Graphite | Graphite	*S. ovata*	3.0	acetate	30%	5.4%	[5]

References for **Table S2**:

[1] E. Schuster, H. G. Schlegel, *Arch. Mikrobiol.* **1967,** *58*, 380.

[2] C. Liu, B. C. Colón, M. Ziesack, P. A. Silver, D. G. Nocera, *Science* **2016,** *352*, 1210.

[3] J. P. Torella, C. J. Gagliardi, J. S. Chen, D. K. Bediako, B. Colón, J. C. Way, P. A. Silver, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2015,** *112*, 2337.

[4] H. Li, P. H. Opgenorth, D. G. Wernick, S. Rogers, T. Y. Wu, W. Higashide, P. Malati, Y. X. Huo, K. M. Cho, J. C. Liao, *Science* **2012,** *335* , 1596.

[5] C. G. S. Giddings, K. P.Nevin, T. Woodward, D. R. Lovley, C. S. Butler, *Front. Microbiol.* **2015,** *6*.