Supporting Information

Bridging Sustainability and Catalytic Efficiency: Cu_7Co Alloy Decorated Biomass-Derived Carbon as a Highly Efficient Electrocatalyst for Hydrogen Generation

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1. Supplementary Notes

Computational Details. All DFT calculations were carried out via the Vienna ab initio Simulation Package (VASP)[1, 2] and the projector augmented wave (PAW) formula.[3, 4] During the structure optimization, the convergence criterion of total energy was set to 1×10^{-7} eV, and the atoms were relaxed until the force acting on each atom was less than 0.03 eV $Å^{-1}$. A plane-wave cutoff energy of 520 eV was used in all computations. Brillouin-zone sampling was sampled with 12 × 12 × 12 Monkhosrt-Pack grid for bulk lattice optimizations and 5 × 5 × 1 for slab model calculations.[5] The lattice constants of Cu were optimized to 3.63 Å. The bottom one layers of three layers were fixed in slab model, and each slab model was separated from its neighbors by a sufficiently thick vacuum layer. A (4 × 4) Cu (111) surface with one surface atom replaced with a Co atom. The binding energies of hydrogen (ΔEH) were obtained from the energies of isolated H_2.

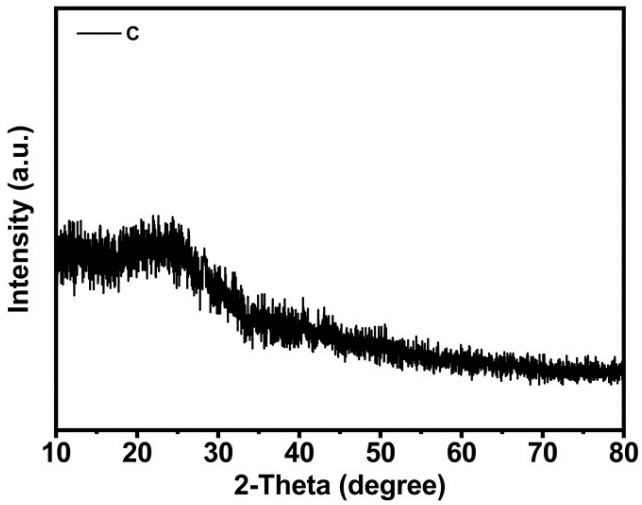

Figure S1. XRD pattern of coconut shell derived carbon.

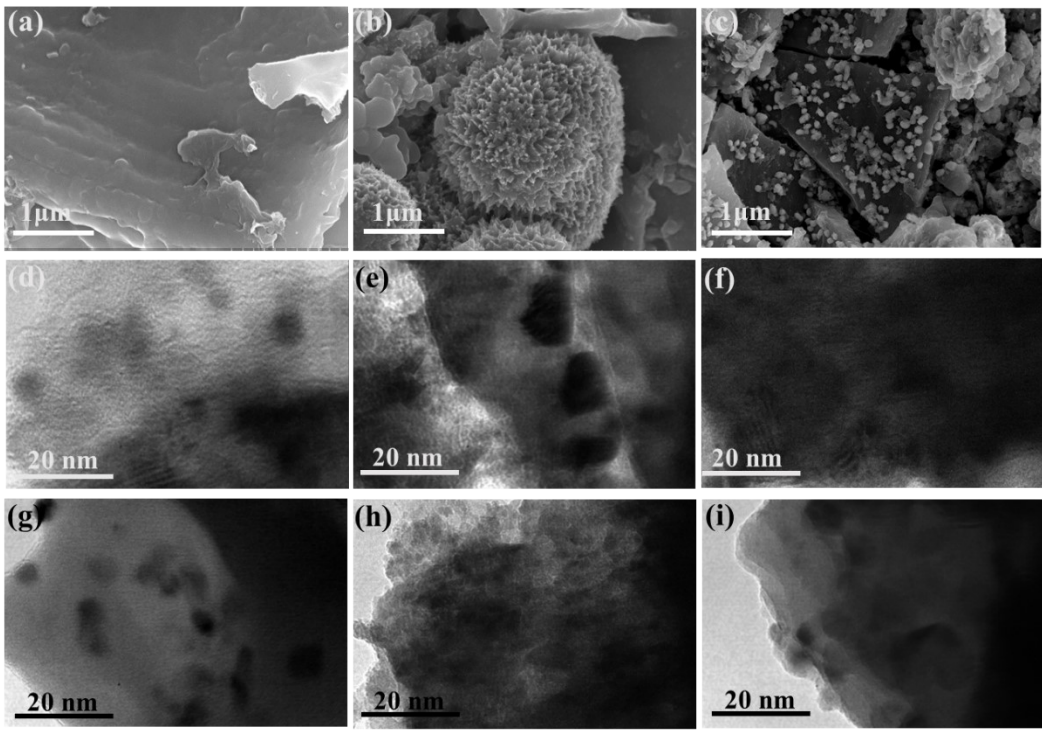

Figure S2. SEM images of (a) C, (b) Co/C, (c) Cu/C, TEM images of (d) $CuCo_3$/C, (e) CuCo/C, (f) Cu_3Co/C, (g) Cu_5Co/C, (h) Cu_7Co/C, and (i) Cu_8Co/C.

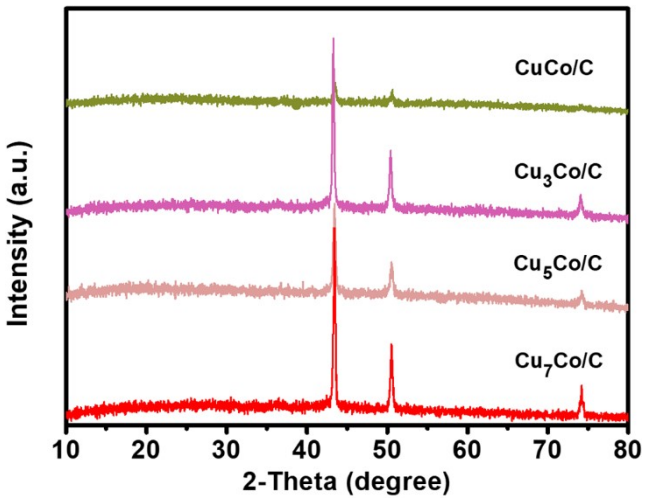

Figure S3. XRD patterns of CuCo/C, Cu_3Co/C, Cu_5Co/C and Cu_7Co/C catalysts.

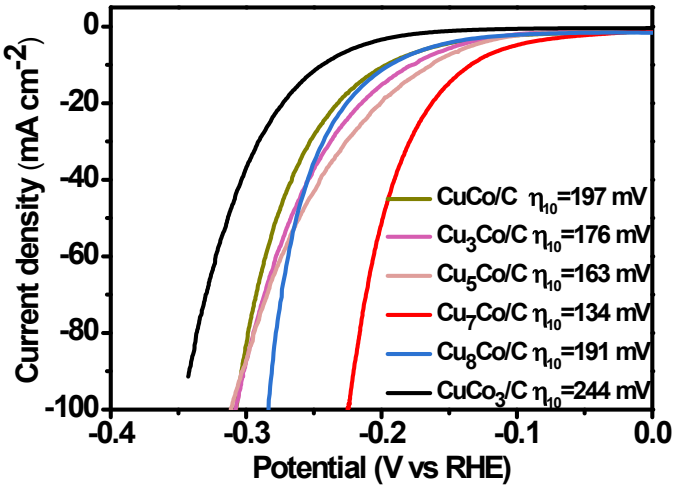

Figure S4. LSV curves of CuCo/C, Cu_3Co/C, Cu_5Co/C, Cu_7Co/C, Cu_8Co/C and $CuCo_3/C$ catalysts in 1.0 M KOH.

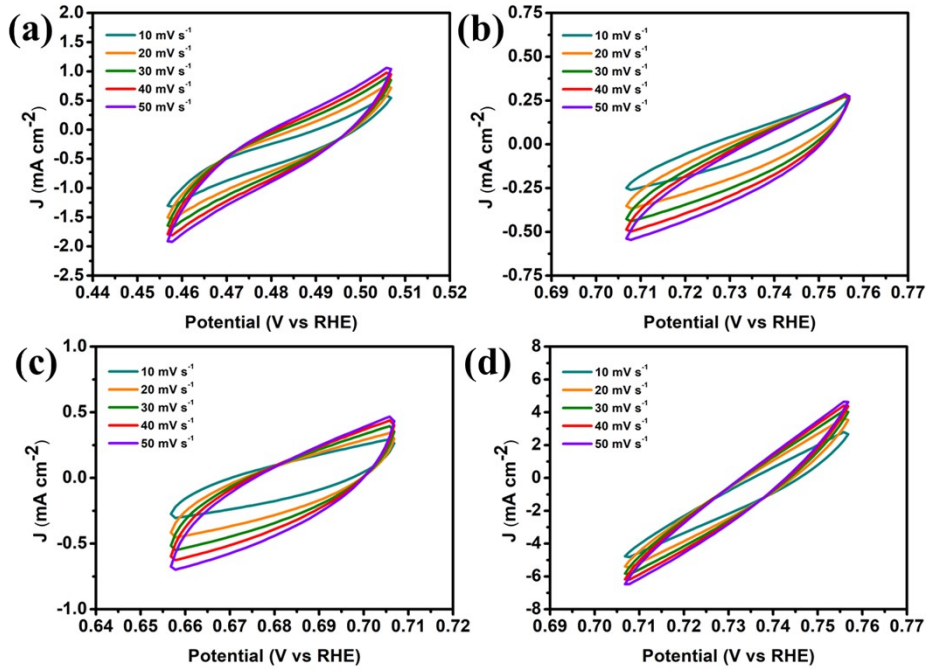

Figure S5. CV curves at different scanning rates of (a) C, (b) Co/C, (c) Cu/C, and (d) Cu_7Co/C.

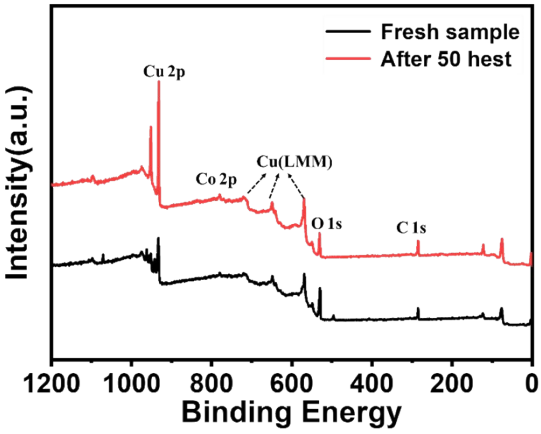

Figure S6. XPS survey spectra of Cu_7Co/C catalyst.

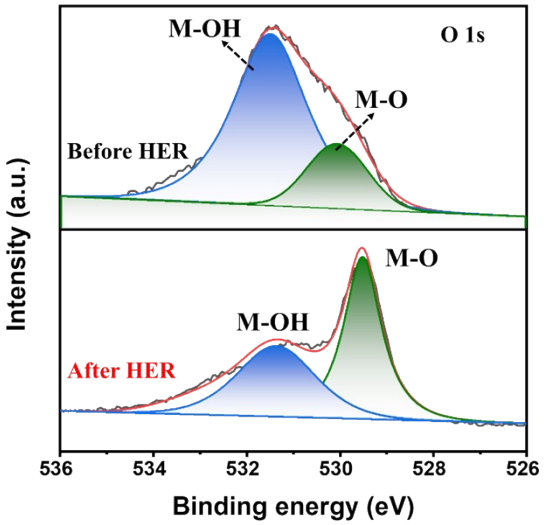

Figure S7. High-resolution XPS spectra of Cu_7Co/C electrode for O 1s.

Table S1. Comparison of HER performances of Metallic carbon-based electrocatalysts reported recently.

Catalyst	η_{10} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	References
Cu_7Co/C	134	94	1.0 M KOH	this work
Ni_3C/CNT	132	49	1.0 M KOH	*Journal of Materials Chemistry A* 2018, 6, 4297-4304.
$Ni_{0.25}Fe_{0.75}$-N, P,S	250	84	1.0 M KOH	*Journal of Power Sources* 2018, 401, 312-321.
NiOx-AC-500	180	121	1.0 M KOH	*Carbon 2020, 157: 515-524.*
Co-CoO/BC yolk-shell	210	93	0.5 M H_2SO_4	*International Journal of Hydrogen Energy* 2019, 44, 6525-6534.
CoS_2/MoS_2/NC	215	80	0.5 M H_2SO_4	*Journal of Alloys and Compounds* 2022, 891, 161962.
PS/MoS_2	154	71	0.5 M H_2SO_4	*Materials Chemistry and Physics* 2020, 252, 123244.
$NiSe_2$@C	206	59	1.0 M KOH	*International Journal of Hydrogen Energy* 2024, 52, 709-717.
Co-Al-O_x/S_y@LSCN	267	23	1.0 M KOH	*Carbon* 2021, 184, 386-399.
Cu/Cu_2OCuO/rGO	118	74	0.5 M H_2SO_4	*Inorganic Chemistry* 2022, 62, 601-608.

Table S2. Calculated H-binding energies (ΔE_H) for Cu (111) and Cu_7Co (111) surfaces.

	No Absorp (eV)	Absorp (eV)	ΔE_H (eV)
Cu	-163.942	-167.535	-0.20946
Cu_7Co	-166.409	-170.303	-0.50972

References

[1] G. Kresse and J. Furthmüller, *Physical review B*, 1996, **54**, 11169.
[2] G. Kresse and J. Hafner, *Physical review B*, 1993, **47**, 558.
[3] J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865.
[4] P. E. Blöchl, *Physical review B*, 1994, **50**, 17953.
[5] H. J. Monkhorst and J. D. Pack, *Physical review B*, 1976, **13**, 5188.