Facile Fabrication of Binary Copper-Palladium Alloy Thin Film Catalysts for Exceptional Hydrogen Evolution Performance

Muhammad Ali Ehsan [a*], Akilarasan Muthumariappan [b], Muhammad Ali [a], Abbas Saeed Hakeem [a], Wasif Farooq [b, c]

[a] Interdisciplinary Research Center-Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum & Minerals, Box 5040, Dhahran 31261, Saudi Arabia.

[b] Interdisciplinary Research Centre for Refining and Advanced Chemicals (IRC-RAC), King Fahd University of Petroleum & Minerals, Dhahran 31261, Kingdom of Saudi Arabia

[c] Department of Chemical Engineering, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, 31261, Saudi Arabia.

*Corresponding author e-mail: meali@kfupm.edu.sa Phone no. +966138607511

Electrochemical measurements

Electrochemical tests were performed using a Gamry potentiostat (Model No: INTERFACE 1010 E. A typical three-electrode system comprising working (as-fabricated CuPd film), reference (Ag/AgCl), and counter (graphite rod) electrodes immersed in 0.5 M H_2SO_4 was used for all measurements. All the measured potentials were normalized with respect to an RHE, as reported in the literature. Activation of catalysts was achieved with cyclic voltammetry (CV) test performed at a scan rate of 50 mV s^{-1}. The HER parameters (overpotential and current density) were analyzed via linear sweep voltammetry (LSV) at a scan rate of 2 mV s^{-1}. A Tafel plot was obtained from the polarization curve using the following equation:

$$\eta = b \, \mathrm{Log}\, j + a, \qquad \text{(Eq. 1)}$$

where *b* is the Tafel slope, and *a* is a constant.

The turnover frequency (TOF) was estimated using the following equation (details are provided in the SI and Table S1):

$$TOF = \frac{j \times A}{4 \times F \times m} \qquad \text{(Eq. 2)}$$

Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 10^5 to 0.1 Hz at an applied potential of –300 mV.

The electrochemically active surface area (ECSA) was calculated using the following formula:

$$\mathrm{ECSA} = C_{dl}/C_s \qquad \text{(Eq. 3)}$$

To determine the double-layer capacitance (C_{dl}), CV curves in the non-Faradic range were recorded at different scan speeds (10–60 mVs^{-1}). The ECSA was obtained by dividing the C_{dl} by the specific capacitance (C_s) of the electrode, as given by Eq. 3. The average specific capacitance in H_2SO_4 solution for metal electrodes is considered as 0.035 mF cm^{-2} in the literature [1].

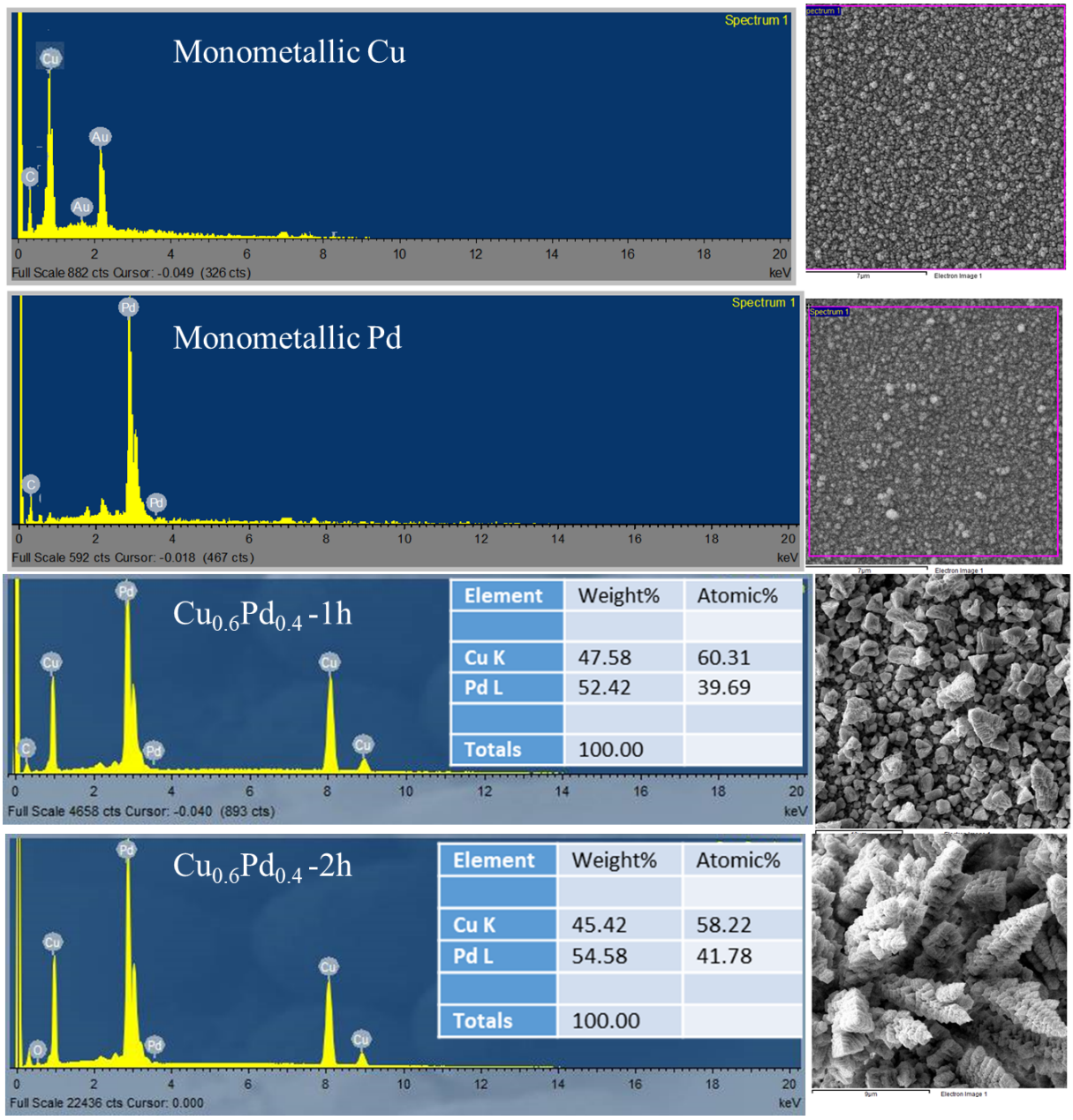

Figure S1. EDX spectra of monometallic Cu, Pd and binary CuPd alloy.

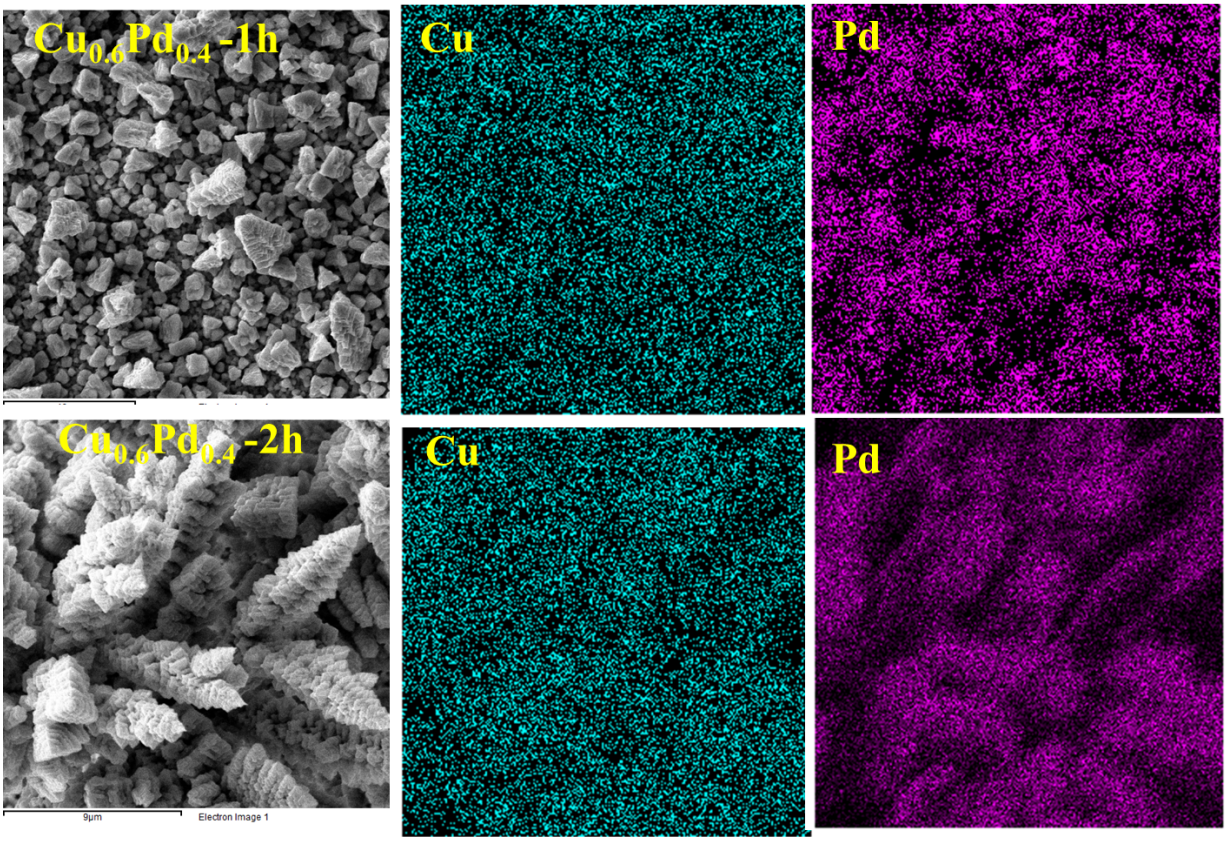

Figure S2. EDX map of binary CuPd alloy samples.

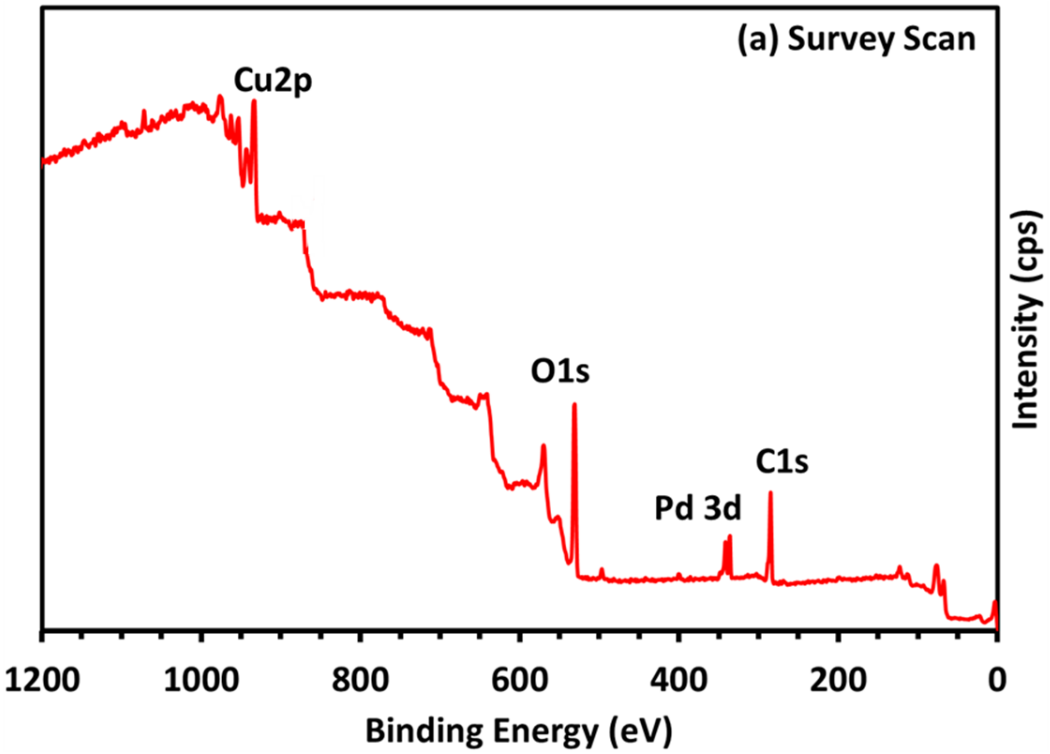

Figure S3. XPS survey scan spectrum of CuPd alloy.

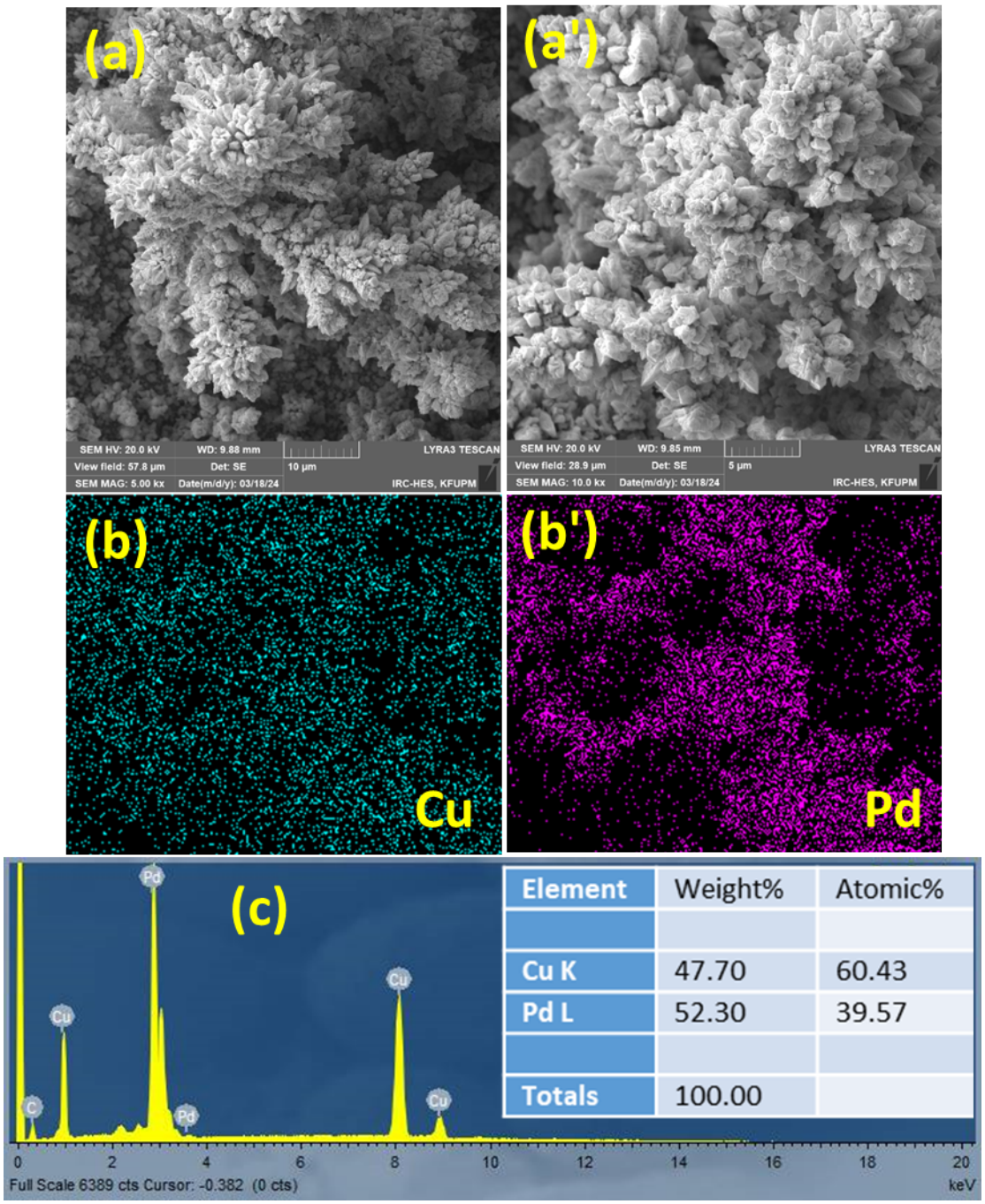

Figure S4. SEM/EDX analysis of binary CuPd-2h electrocatalyst after stability test.

Table S1: Comparison of the HER performance conducted in 1.0 M H_2SO_4 electrolyte of various Pd based electrocatalysts synthesized via different methods.

Catalysts	**Synthesis route**	**Substrate**	**Overpotential**	**Tafel Slope**	**Ref.**
PdCo@CN	MOF annealing	GCE	80	31	2
Pd_xCu_{100-x}/C	one-pot synthesis	GCE	102	48	3
Pd/Bi/Cu HNAs	electrodeposition	GCE	79	61	4
PdCu NPs/SBA-15-MWCNT	Solution processing	carbon paste electrode	150	45	5
Pt@Pd	one-pot synthesis	GCE	56	39	6
PdTe	hydrothermal method followed by reduction	GCE	97	90	7
PdNi NWs	template-confined electrodeposition	GCE	91	96	8
PdCo@N–C/rGO	MOF/graphene oxide pyrolysis	GCE	87	66	9
$Cu_{0.6}Pd_{0.4}$-2h	AACVD	Graphite sheet	20	28	**This Work**

References

[1] C.C. McCrory, J. Suho, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo "Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices." *J. Am. Chem. Soc*. **2015**, *137*, 4347-4357.
[2] J. Chen, G. Xia, P. Jiang, Y. Yang, R. Li, R. Shi, R, R. Shi, J. Su and Q. Chen "Active and durable hydrogen evolution reaction catalyst derived from Pd-doped metal–organic frameworks" *ACS Appl. Mater. Interfaces* **2016**, *8*, 13378-13383.
[3] X. Zhang, W. Dengfeng and D. Cheng "Component-dependent electrocatalytic activity of PdCu bimetallic nanoparticles for hydrogen evolution reaction." *Electrochim. Acta* **2017**, *246*, 572-579.
[4] L. Zheng, Z. Shizheng, W. Hongrui, L. Du, Z. Zhu, J. Chen, and D. Yang. "Palladium/bismuth/copper hierarchical nano-architectures for efficient hydrogen evolution and stable hydrogen detection." *ACS Appl. Mater. Interfaces* **2019**, *11*, 6248-6256.
[5] E. Chiani, S. N. Azizi, and S. Ghasemi "PdCu bimetallic nanoparticles decorated on ordered mesoporous silica (SBA-15)/MWCNTs as superior electrocatalyst for hydrogen evolution reaction." *Int. J. Hydrogen Energy* **2021**, *46*, 25468-25485.
[6] X-X Lin, A-J. Wang, K-M. Fang, J. Yuan, and J.-Ju Feng "One-pot seedless aqueous synthesis of reduced graphene oxide (rGO)-supported core–shell Pt@ Pd nanoflowers as advanced catalysts for oxygen reduction and hydrogen evolution." *ACS Sustain. Chem. Eng.* **2017**, *5*, 8675-8683.
[7] L. Jiao, L. Feng, L. Xinzhe, R. Ren, J. Li, X. Zhou, J. Jin, and R. Li "Ultrathin PdTe nanowires anchoring reduced graphene oxide cathodes for efficient hydrogen evolution reaction." *Nanoscale* **2015**, *7*, 18441-18445.
[8] L. Du, D. Feng, X. Xing, C. Wang, G. S. Armatas, and D. Yang "Uniform palladium-nickel nanowires arrays for stable hydrogen leakage detection and efficient hydrogen evolution reaction". *Chem. Eng. J*. **2020**, *400*, 125864.
[9] M. Zhong, L. Lingling, K. Zhao, F. He, B. Su, and D. Wang. (2021). "PdCo alloys@ N-doped porous carbon supported on reduced graphene oxide as a highly efficient electrocatalyst for hydrogen evolution reaction" J. Mater. Sci. **2021**, *56*, 14222-14233.