Supporting Information

Facile Synthesis of Ni–Cu Composite Reinforced with a Para-Phenylenediamine Layer for Enhanced Hydrogen Evolution Reaction

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I. Effect of the electrodeposition mode of pPD

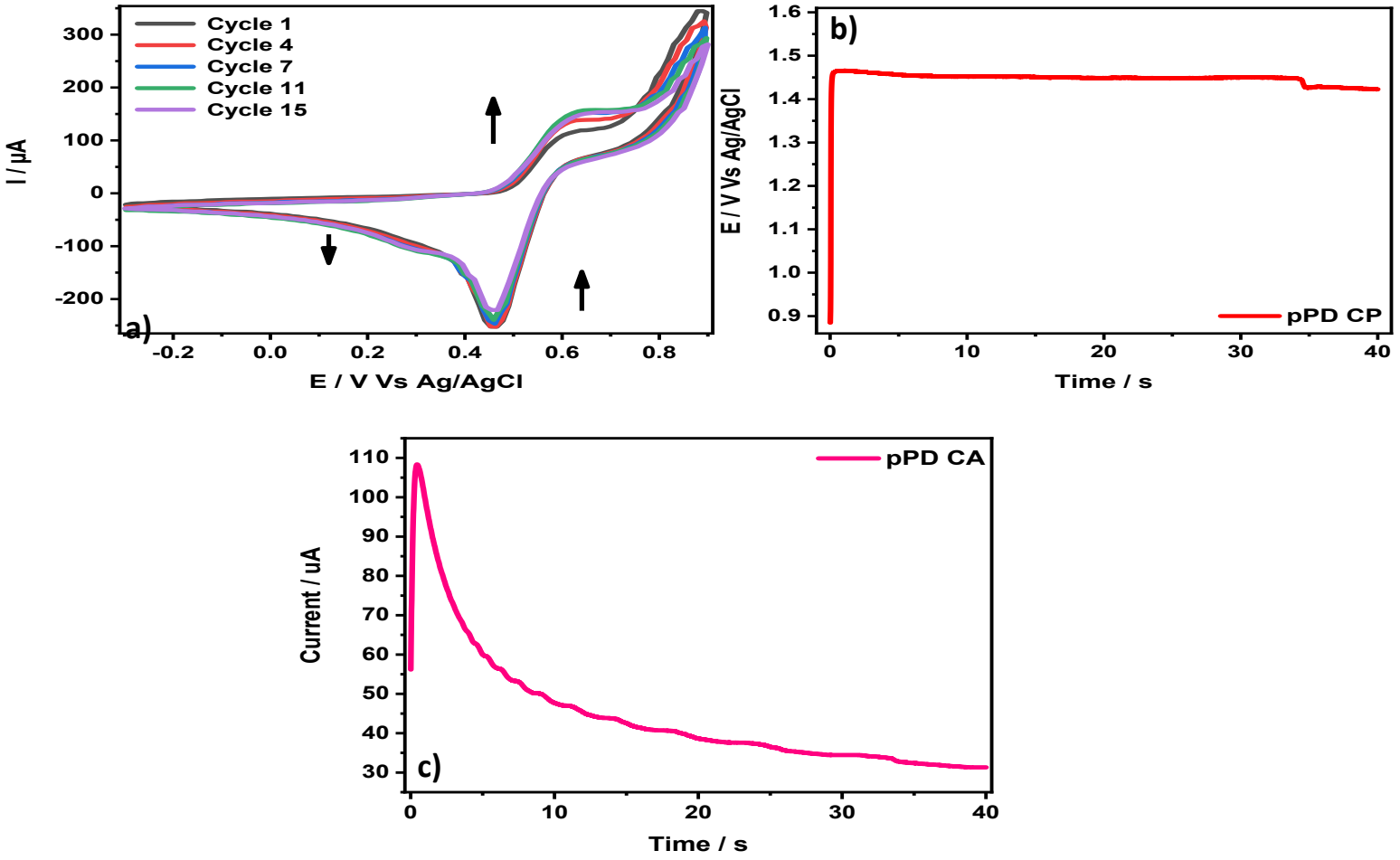

Fig. S1: electrodeposition of pPD on CPE by a) Cyclic Voltammetry b) Chronopotentiometry c) Chronoamperometry

Once the film of polymer was prepared using different mode of electrodeposition, the electrochemical responses towards ferri-ferrocyanure system were investigated for comparative purposes. In this perspective, CV measurements were performed in 100 mM KCl containing 1 mM $[Fe(CN)_6]^{3-/4-}$ on different electrodes. As depicted in Fig.S2, the peak-to-peak separation on CPE (black line) is equal to 428 mV, which indicate a slow electron transfer[1]. On the $(CPE/pPD)_{CV}$, the peak-to-peak separation was reduced to reach the value of 196 mV (red line) and the current intensities increased by about 45 %. This behavior could be explained by the high electrical conductivity and a large specific surface area offered by the polymer. The same phenomena was observed by Oularbi et al. (2017) [2]. It is important to note that after the electrodeposition of para-phenylenediamine on CPE by CA and CP methods (green and blue line respectively), the peak-to-peak separation was decreased at the value of ΔEp equal 82 mV and 121 mV respectively due to the improvement of the electron transfer at the interface electrode-solution and the current intensities increased by about 97 % and 65 % respectively.

The increasing percentage was calculated as follows [3].

$$\%(Increase) = \frac{Ipa\ (CPE\ /pPD) - Ipa\ (CPE)}{Ipa\ (CPE)}$$

Table S1 summarize the obtained results, i.e., the current densities of the anodic peak Ip_a and cathodic peak Ip_c and also the peak-to-peak separation. According to these findings, the chronoamperometry (CA) method was relied upon for the deposition of the pPD in the rest of the work.

Table S1: **Comparison between Ipa, Ipc and the peak-to-peak separation (ΔEp) for CPE, CPE / pPD CV, CPE / pPD CP, CPE / pPD CA**

Electrode	Ipa µA	Ipc µA	Epa mV	Epc mV	peak-to-peak▲Ep (mV)	increasing percentage (current)
CPE	10.78	-11,2	418	-10	428	-------
CPE / pPD CV	15,69	-15,71	303	107	196	45 %
CPE / pPD CP	17,85	-18,93	278	157	121	65 %
CPE / pPD CA	21,27	-22,46	260	178	82	97 %

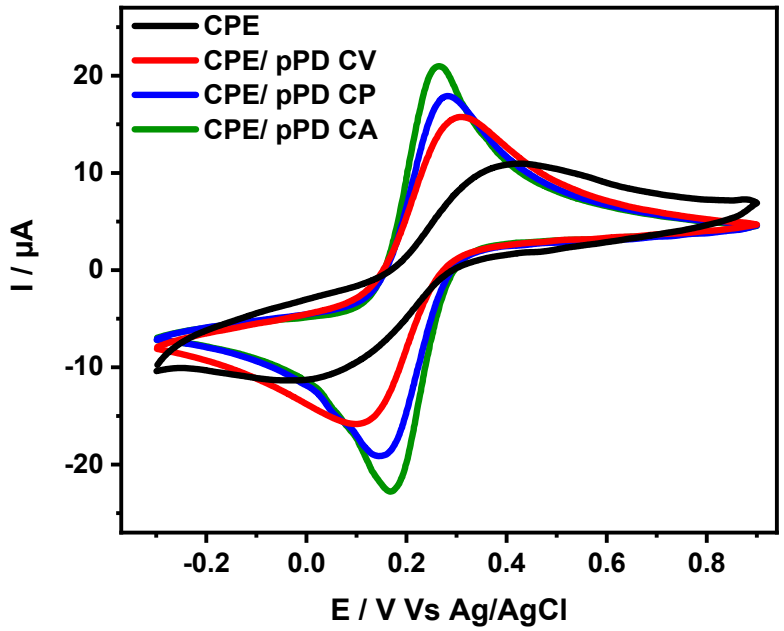

Fig. S2: CV of CPE (black line), CPE/pPD by CV (red line), and CPE/pPD by CP (blue line), and CPE/pPD by CA (green line) in 0.1 M of KCl containing 1 mM of $[Fe(CN)6]^{3-/4-}$ at scan rate 0.05 V/s.

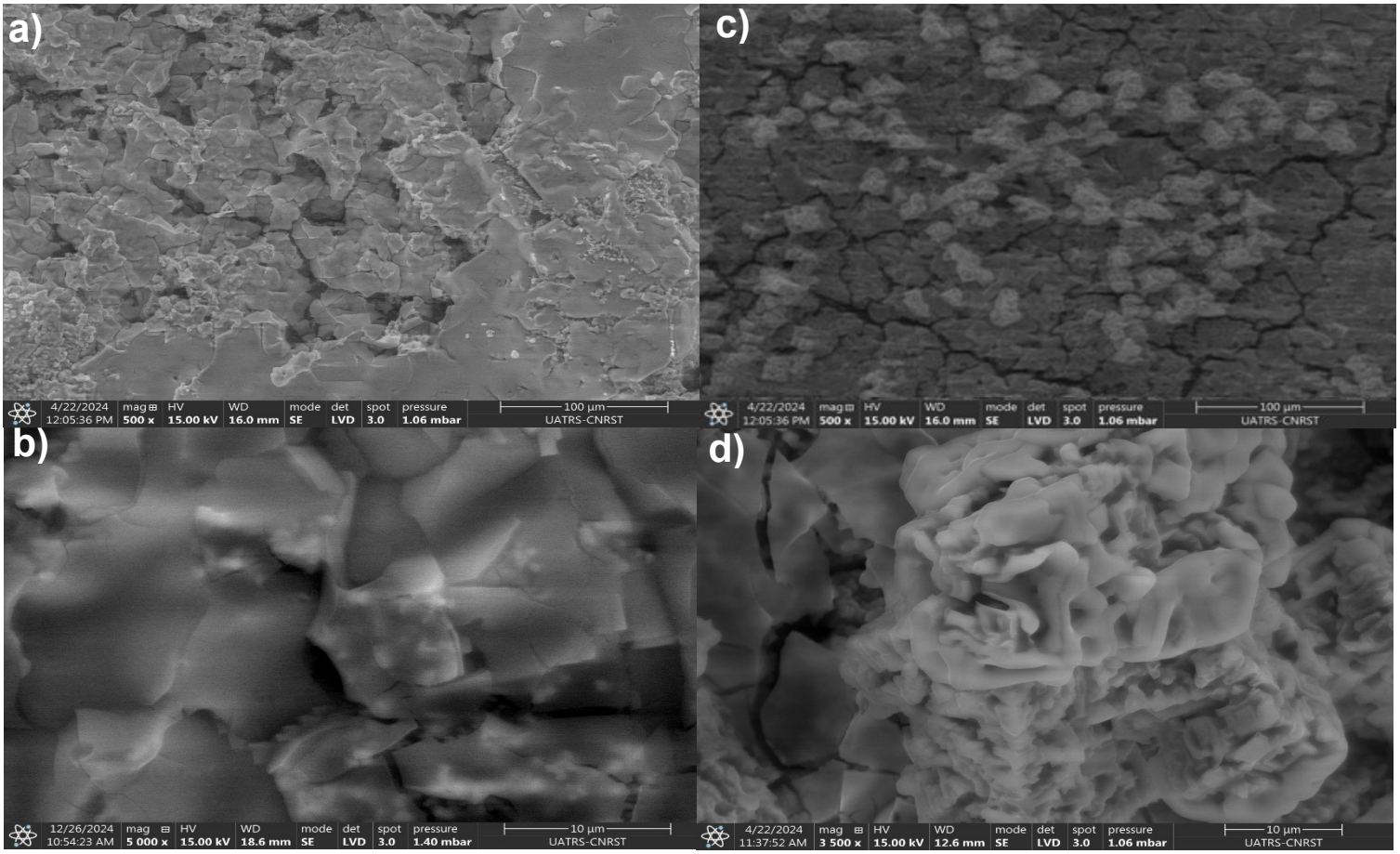

Fig. S3: SEM photographs of the Ni_4Cu_1 deposit on a, b) pPD deposit by potentiostatic mode, c, d) pPD deposit by cyclic voltammetry.

II. Effect of the electrodeposition mode of Nickel Copper particles

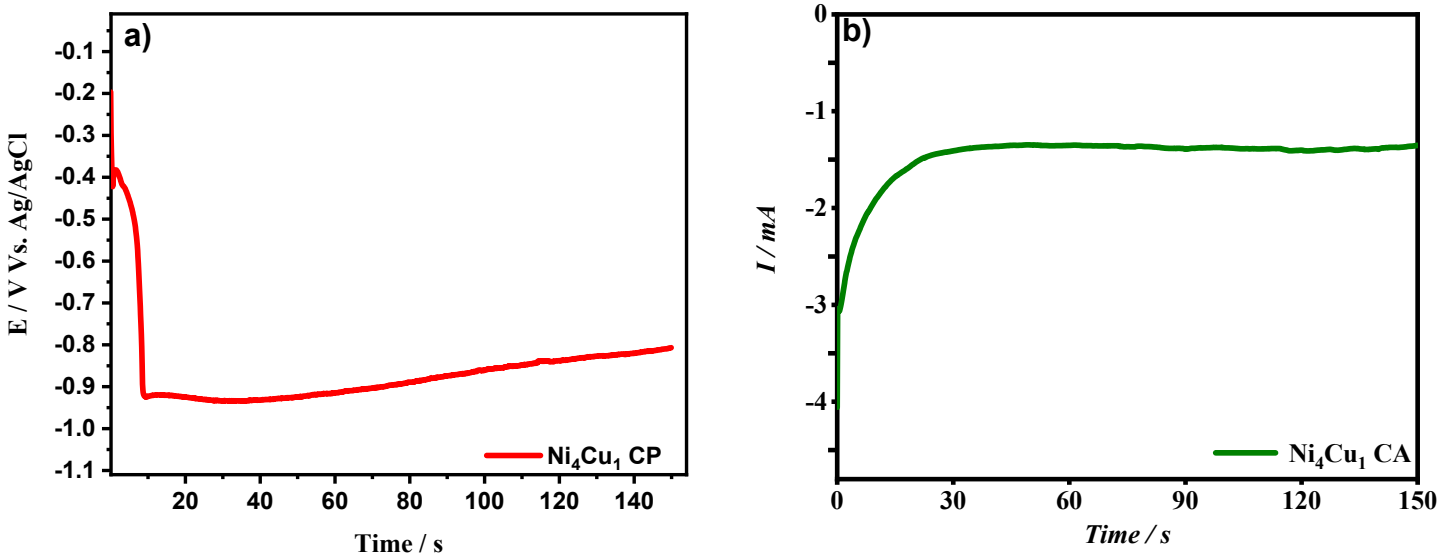

Fig. S4: a) Chronopotentiometry curve of the deposition of Ni_4Cu_1 at -3 mA. b) Chronoamperometry curve of the deposition of Ni_4Cu_1 at – 0.9 V vs. Ag/AgCl.

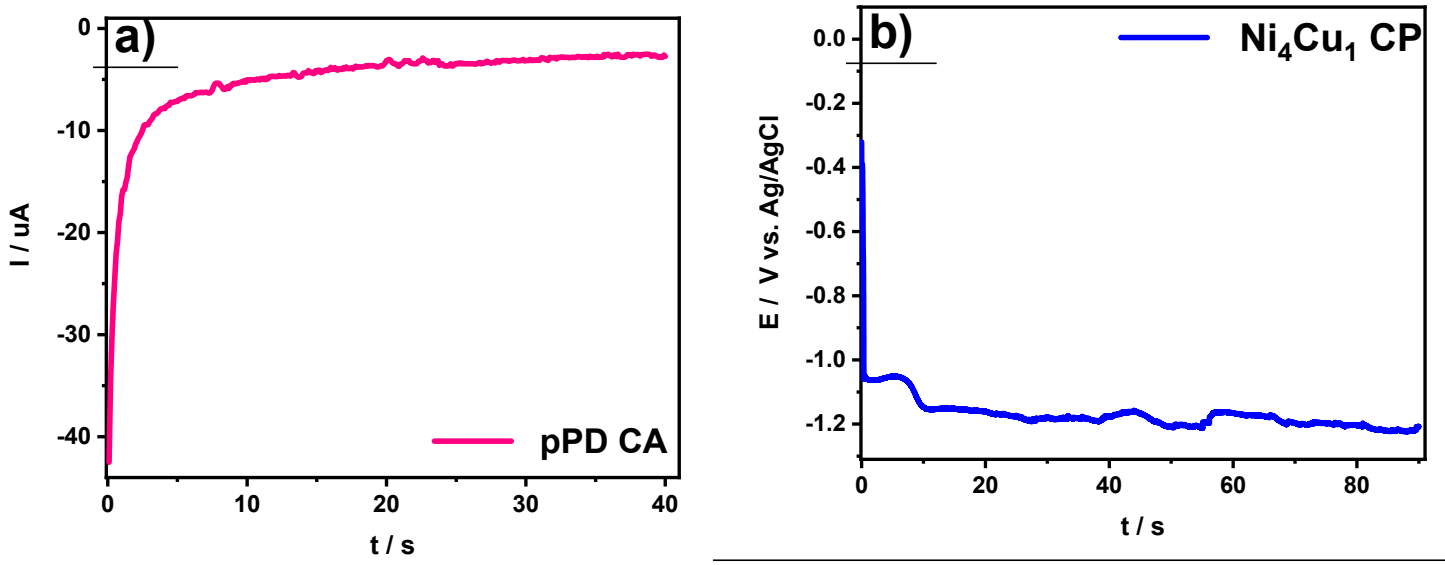

Fig. S5: a) Electrodeposition of pPD on CPE by Chronoamperometry 0V during 40s. b) Chronopotentiometry curve of the deposition of Ni_4Cu_1 at -4 mA during 90s on the prepared pPD/CPE electrode.

III. Electrocatalytic performance of the electrocatalysts on HER

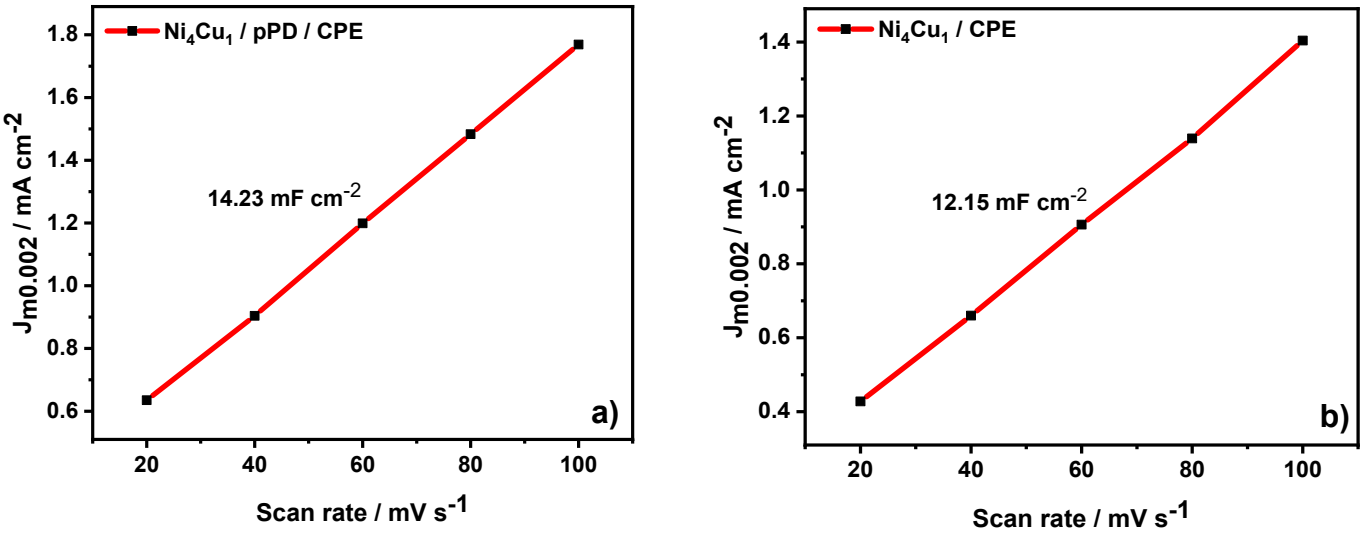

Fig. S6: The relationship between the current density and the scanning speed of (a) Ni_4Cu_1/pPD/CPE and (b) Ni_4Cu_1/CPE.

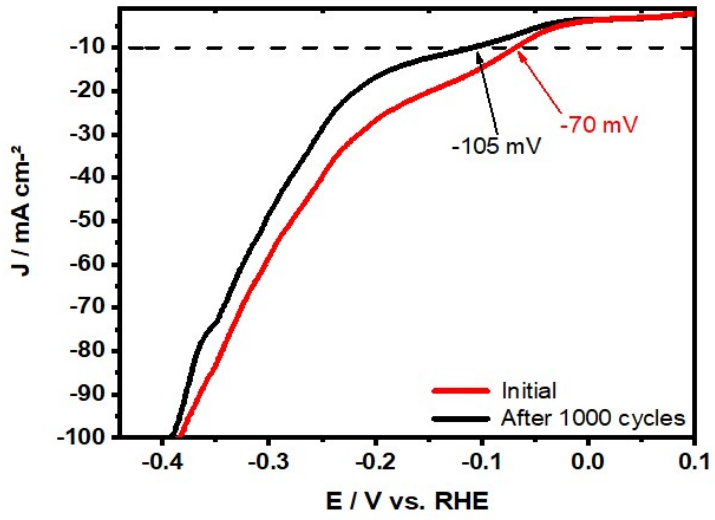

Fig. S7: Polarization curves initially and after 1000 electrolysis of the electrocatalyst Ni_4Cu_1/pPD/CPE at -10 mA cm^{-2} in alkaline media 1M KOH.

Reference

1 O. Salhi, T. Ez-zine, L. Oularbi and M. El Rhazi, *Front. Chem.*, 2022, **10**, 870393.

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3 S. Chemchoub, M. Elbasri, El. M. Halim and M. El Rhazi, *Materials Today: Proceedings*, 2019, **13**, 720–729.