

# SUPPORTING INFORMATION OF

## Green and easy synthesis of P-doped carbon-based hydrogen evolution reaction electrocatalysts

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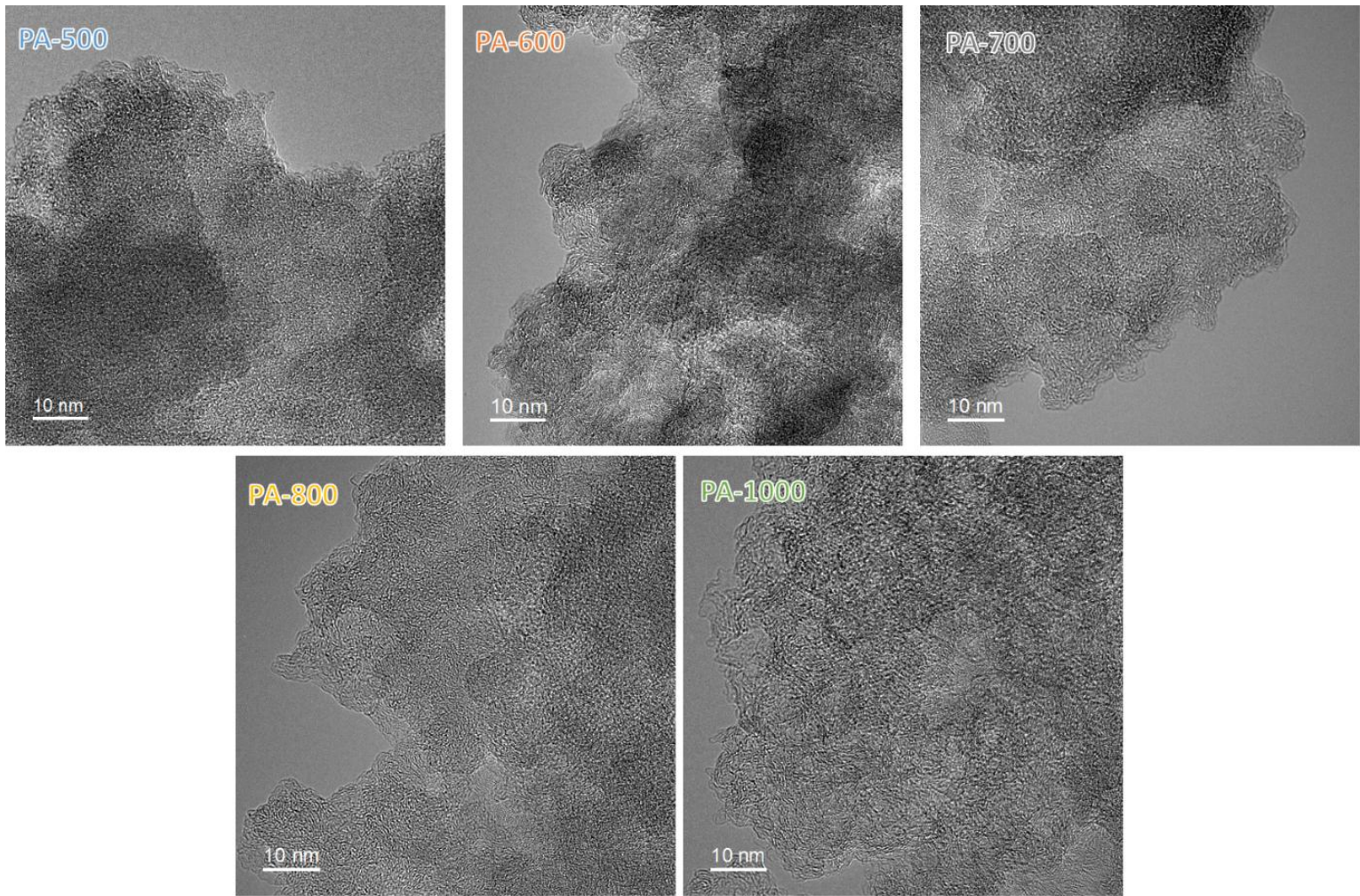


Figure S1: TEM images of PA-500, PA-600, PA-700, PA-800 and PA-1000.

	at%	at%	at%	-
<b>PA-500</b>	47.1	36.3	16.7	0
<b>PA-600</b>	48.5	35.2	16.3	0
<b>PA-700</b>	49.6	34.7	15.7	0.11
<b>PA-800</b>	72.4	19.5	8.1	0.52
<b>PA-900</b>	82.7	13.2	4.0	0.80
<b>PA-1000</b>	86.2	10.9	2.9	0.66

Table S1: Atomic percentages (at.%) of carbon (C), oxygen (O) and phosphorus (P), as well as P-C/P<sub>T</sub> ratio, obtained by XPS, for all PA-x materials.

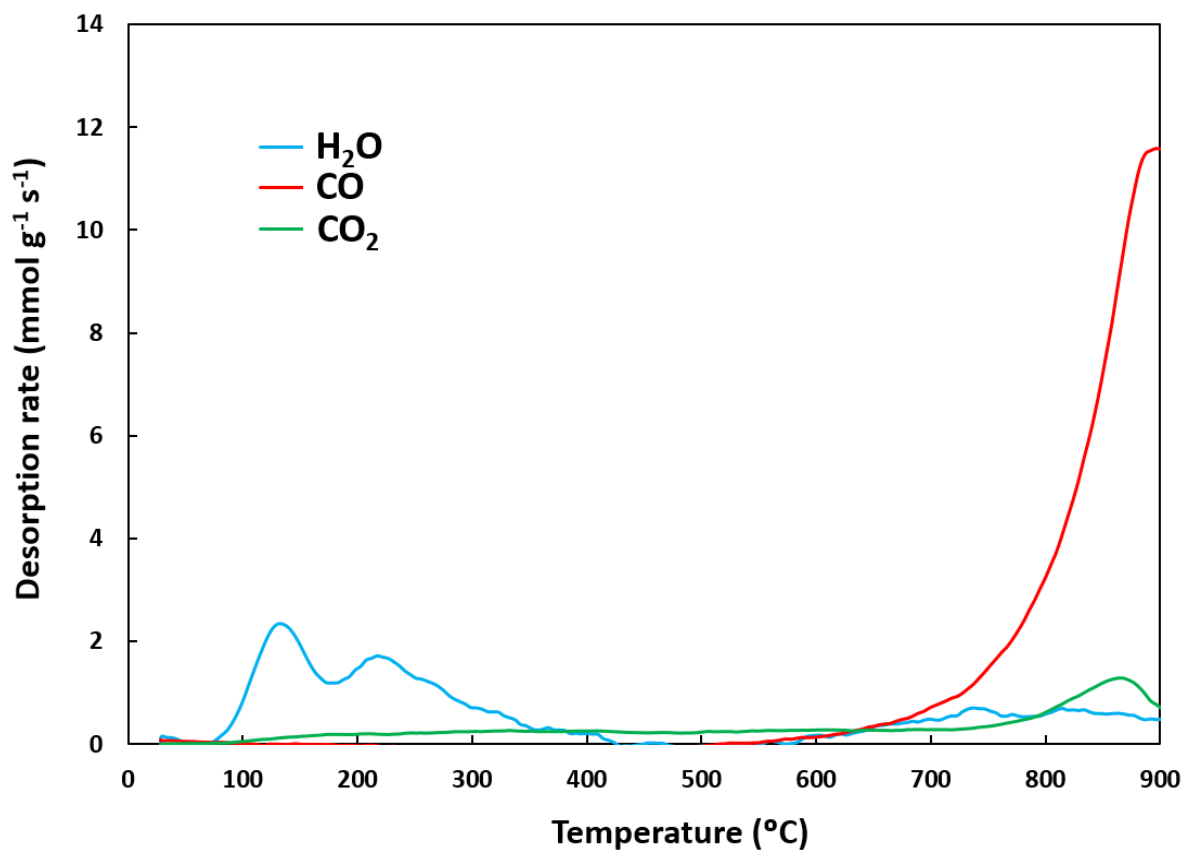


Figure S2: Temperature programmed desorption results obtained from PA-900 following the m/z lines of 18 ( $\text{H}_2\text{O}$ ), 28 ( $\text{CO}$ ) and 44 ( $\text{CO}_2$ ).

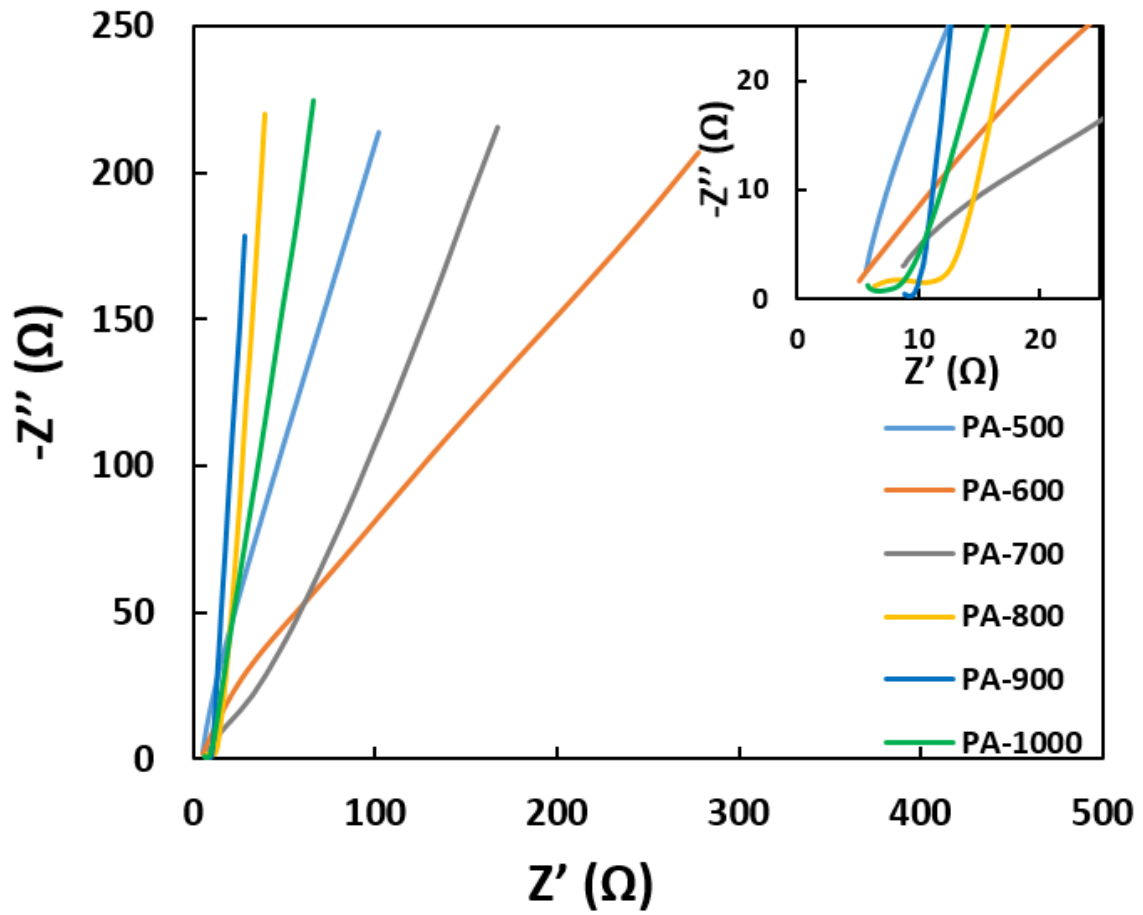


Figure S3: Electrochemical impedance spectra (EIS) of all P-doped carbons, an inset of the EIS plot focusing on the 25-25  $\Omega$  range is located in the top right corner.

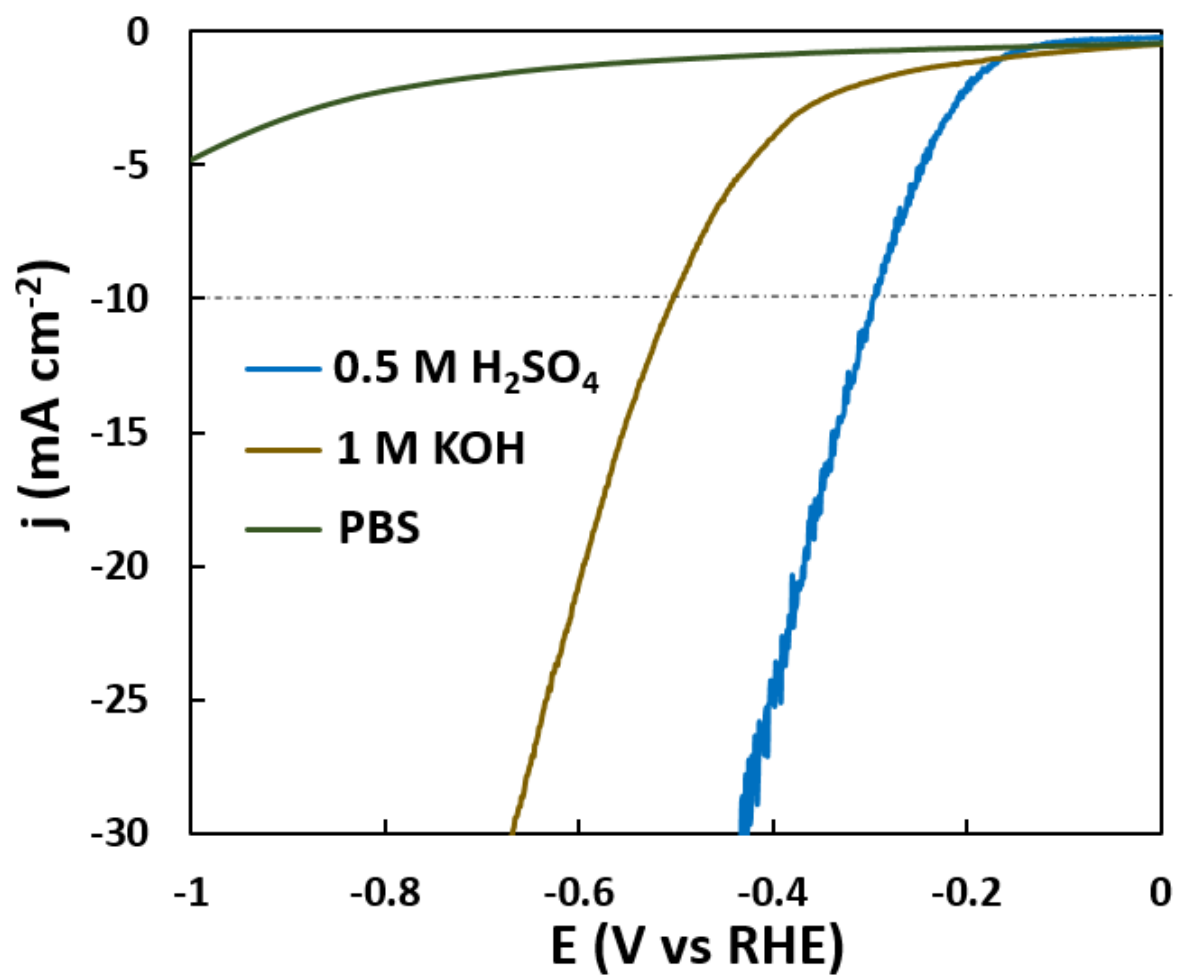


Figure S4: Linear sweep voltammeteries in  $\text{N}_2$ -saturated solution of PA-900 in acid (0.5 M  $\text{H}_2\text{SO}_4$ ), basic (1 M  $\text{KOH}$ ) and neutral (PBS) media at  $50 \text{ mV s}^{-1}$ .



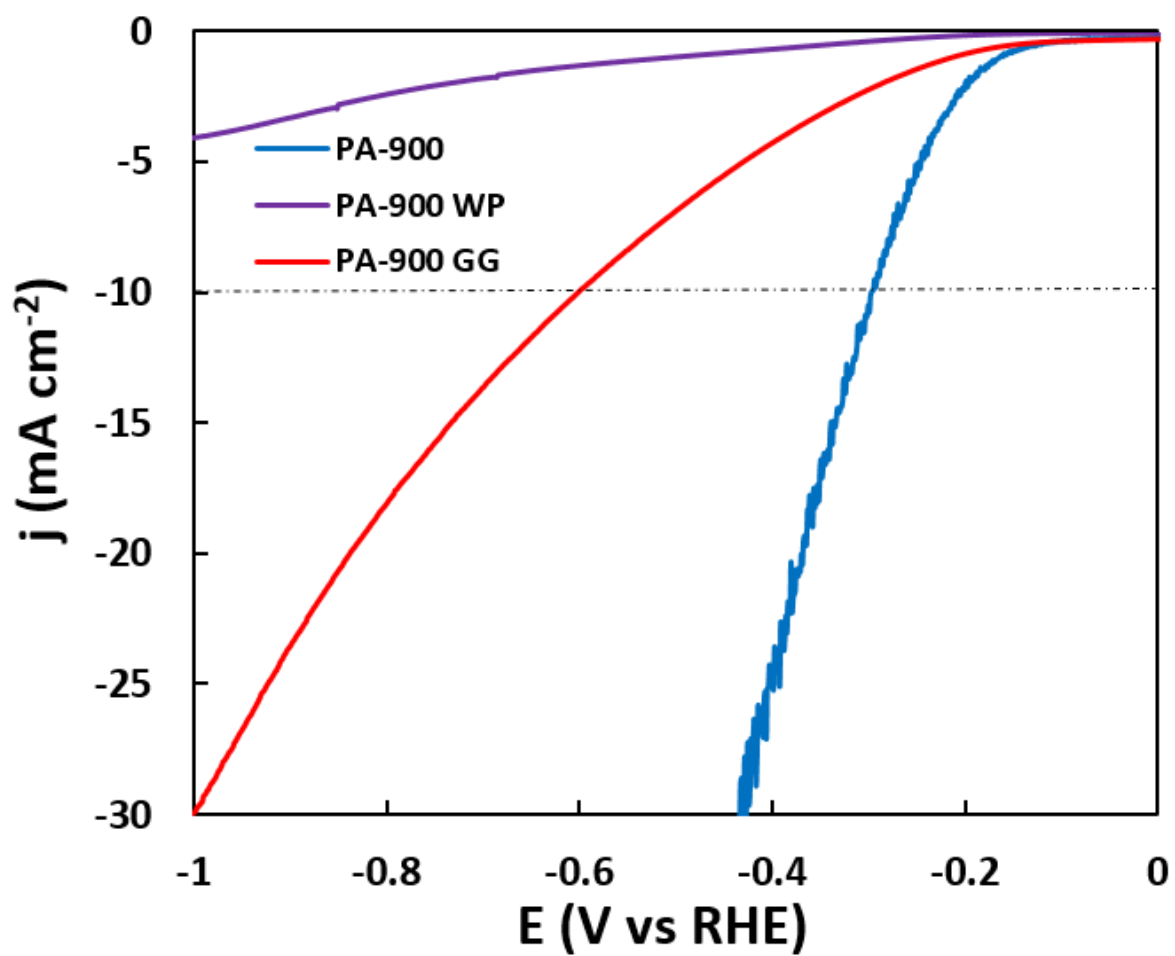


Figure S5: Linear sweep voltammograms in a 0.5 M H<sub>2</sub>SO<sub>4</sub>, N<sub>2</sub>-saturated solution at 50 mV s<sup>-1</sup> of PA-900, PA-900 WP and PA-900 GG.



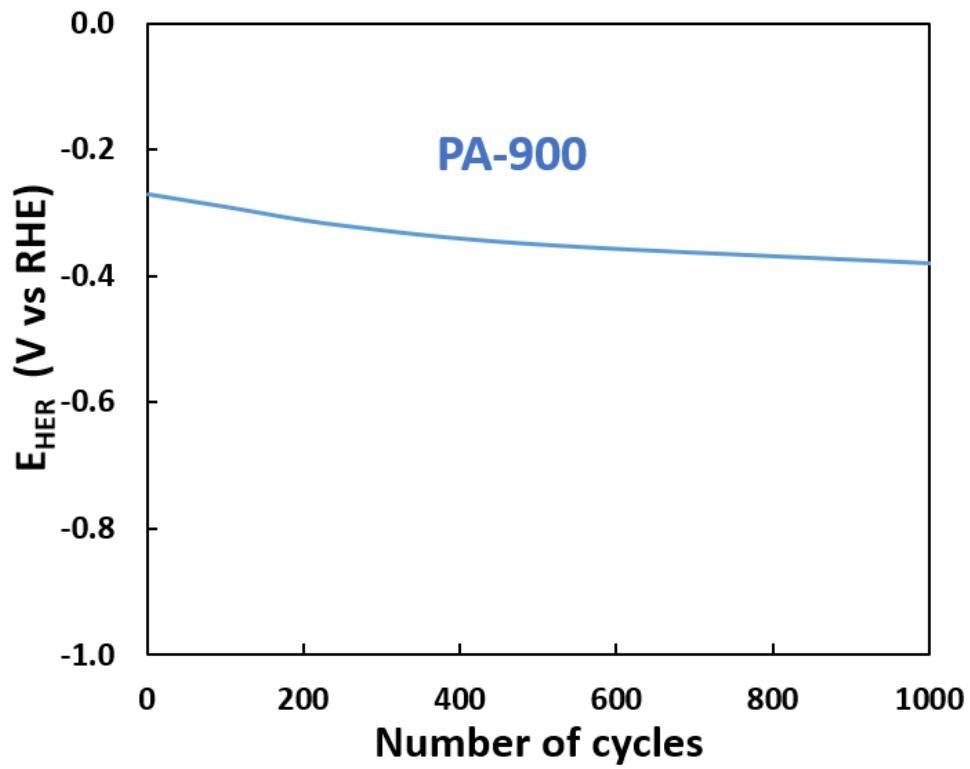


Figure S6: Study of the stability of PA-900 during 1000 cycles under working conditions.

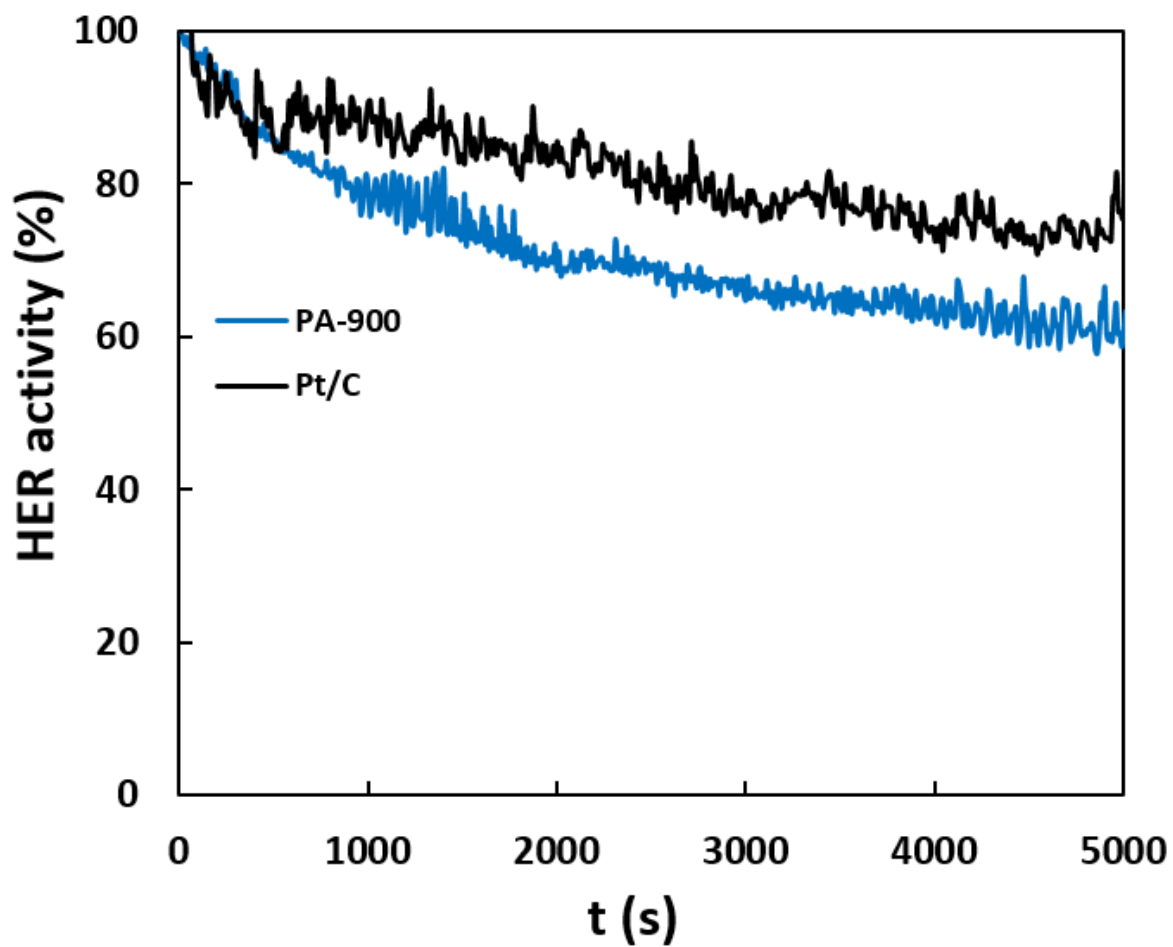


Figure S7: Chronoamperometric analysis at a fixed potential of -0.24 V vs RHE for PA-900 and -0.01 V for Pt/C catalysts.

Table S2: Literature comparison of the performances of materials shown in Figure 5f and similar to PA-900 for the HER. Red color means N heteroatoms, green color means P heteroatoms and black means no heteroatoms

Material	Material description	$\eta$ (mV)	SA (m <sup>2</sup> g <sup>-1</sup> )	Reference
<b>C<sub>3</sub>N<sub>4</sub></b>	Carbon Nitride	-0.24	240	[S1]
<b>P-doped carbon</b>	P-doped carbon	-0.30	300	[S2]
<b>PDGSL1</b>	P-containing graphite layers	-0.31	310	[S3]
<b>PDGLS2</b>	P-containing graphite layers	-0.32	320	[S3]
<b>PDGLS3</b>	P-containing graphite layers	-0.34	340	[S3]
<b>PDGLS4</b>	P-containing graphite layers	-0.40	400	[S3]
<b>PDGLS5</b>	P-containing graphite layers	-0.43	430	[S3]
<b>NC/CNT</b>	N-doped carbon/multi-walled carbon nanotubes	-0.57	574	[S4]
<b>CNT</b>	Carbon Nanotube	-0.62	620	[S5]
<b>PC</b>	Phosphorus-doped carbon	-1.00	1000	[S6]

## References

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