Electronic Supplementary Material (ESI) for Nanoscale.

## *Supporting Materials*

# *Rugae-Like FeP Nanocrystal Assembly on Carbon Cloth: An Exceptionally Efficient and Stable Cathode for Hydrogen Evolution*

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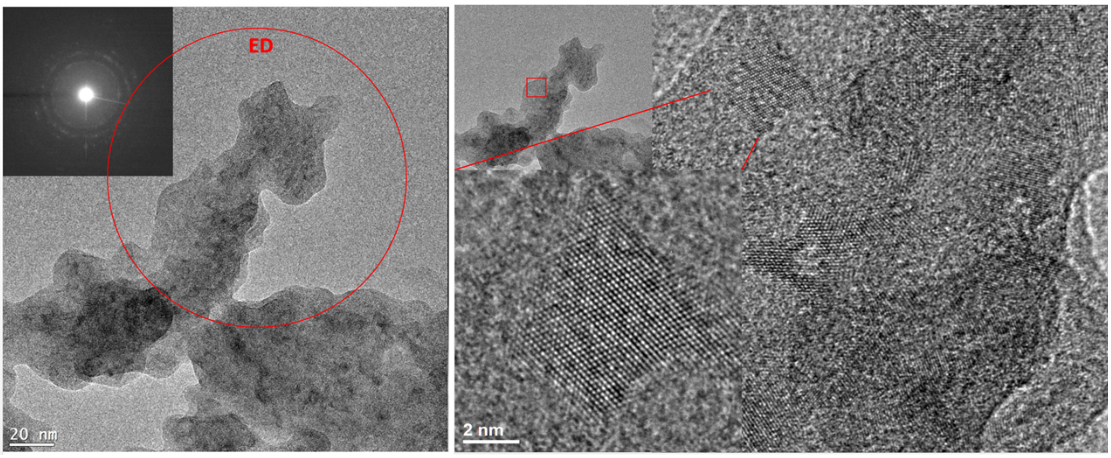

**Fig. S1** TEM images for the FeP phosphidated at 250 °C. Electron diffraction (ED) reveals that these crystallites are randomly oriented.

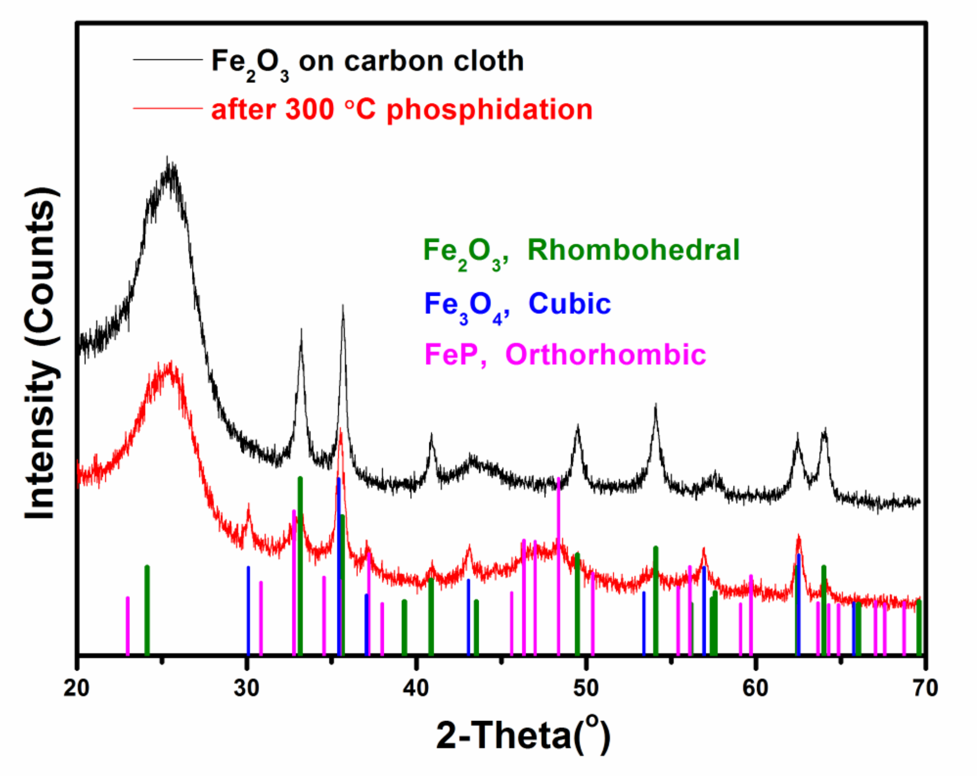

**Fig. S2** XRD pattern of the $Fe_2O_3$ on carbon cloth obtained after heating the electroplated FeOOH at 400 °C in air for 4 h. The red curve is the XRD pattern for the sample after phosphidation at 300 °C for 1 h. Only some portion of the $Fe_2O_3$ is converted to $Fe_3O_4$ and FeP.

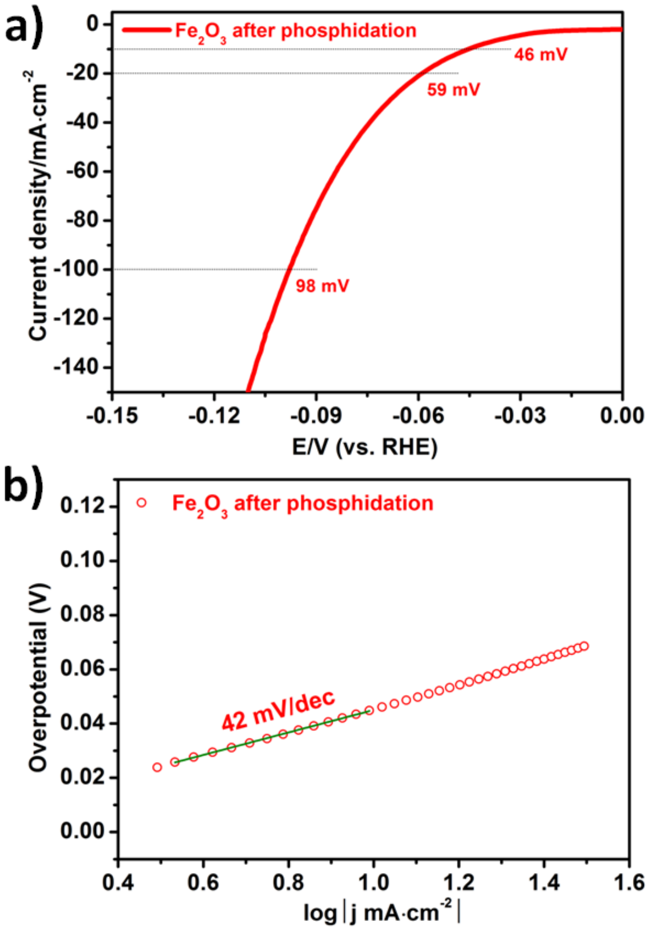

**Fig. S3** (a) Polarization curves for the $Fe_2O_3$ on carbon cloth after 300 $^{o}$C phosphidation, where the over potential to reach 10 and 20 mA/cm$^2$ is 46 and 59 mV respectively. (b) The Tafel slope for the sample is 42 mV/dec.

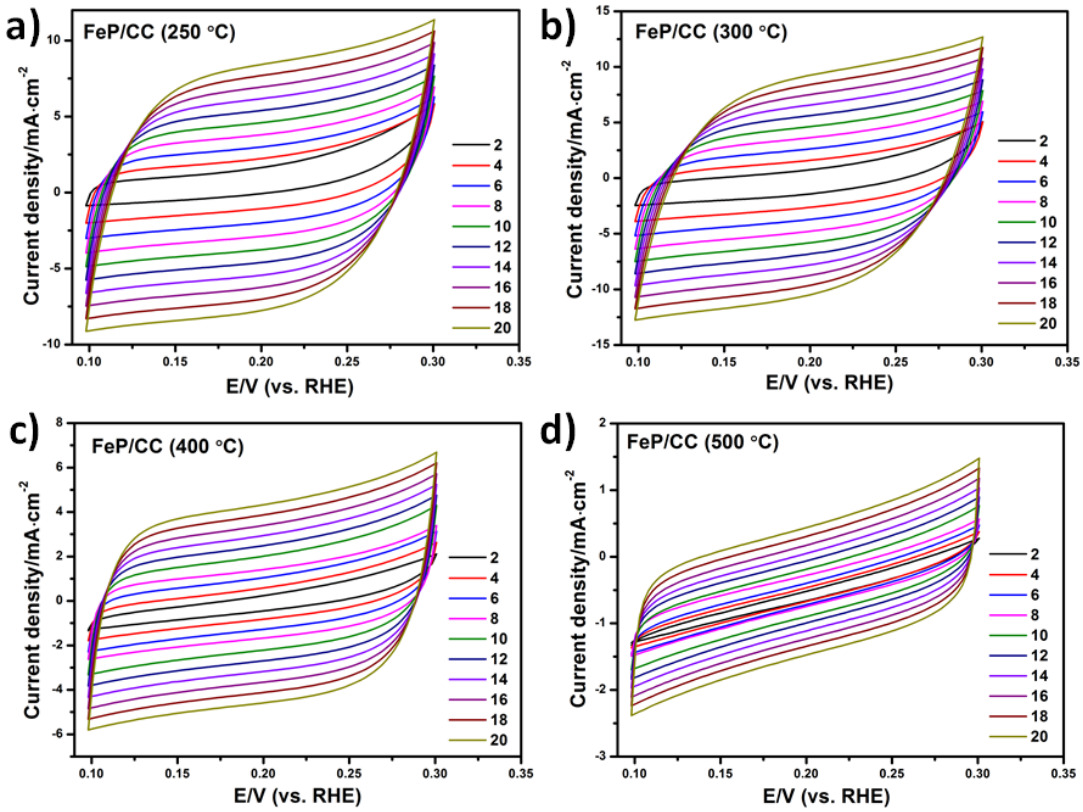

**Fig. S4** Cyclic voltammograms (CV) of FeP catalysts prepared at different phosphidation temperatures, where the curves are taken in a potential window without faradaic processes in a 0.5 M $H_2SO_4$.

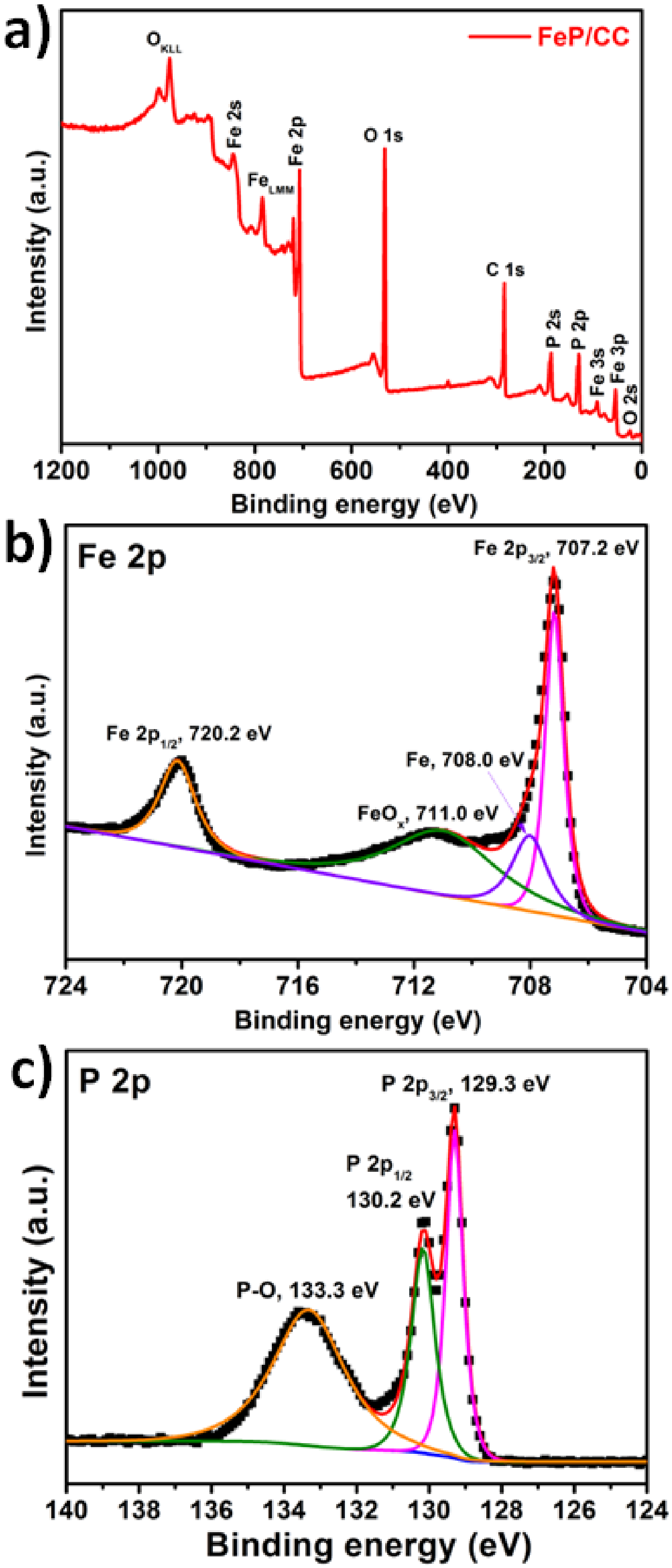

**Fig. S5** (a) XPS survey spectrum of the FeP/CC. High resolution XPS spectra showing the binding energies of the (b) Fe 2p and (c) P 2p obtained from the FeP/CC sample.

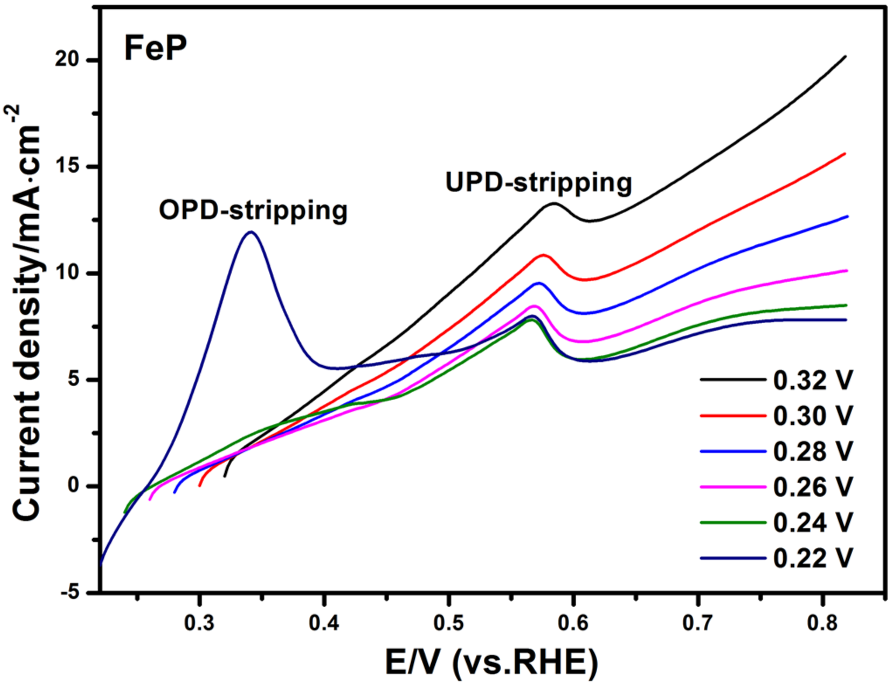

**Fig. S6** After the UPD of Cu on FeP catalysts at various underpotentials (0.22, 0.24, 0.26, 0.28, 0.30 and 0.32 V), linear voltammetric scans were then performed from the set underpotential to a point at which all of the UPD copper had been oxidized at a scan rate of 5 mV·s$^{-1}$. It is observed that curves for the UPD at 0.22V and 0.24V show an OPD-stripping peak, meaning that some over potential-deposited Cu is involved. The curve for UPD at 0.26V is used to extract the charge quantity $Q_{Cu}{}^{2+}$.

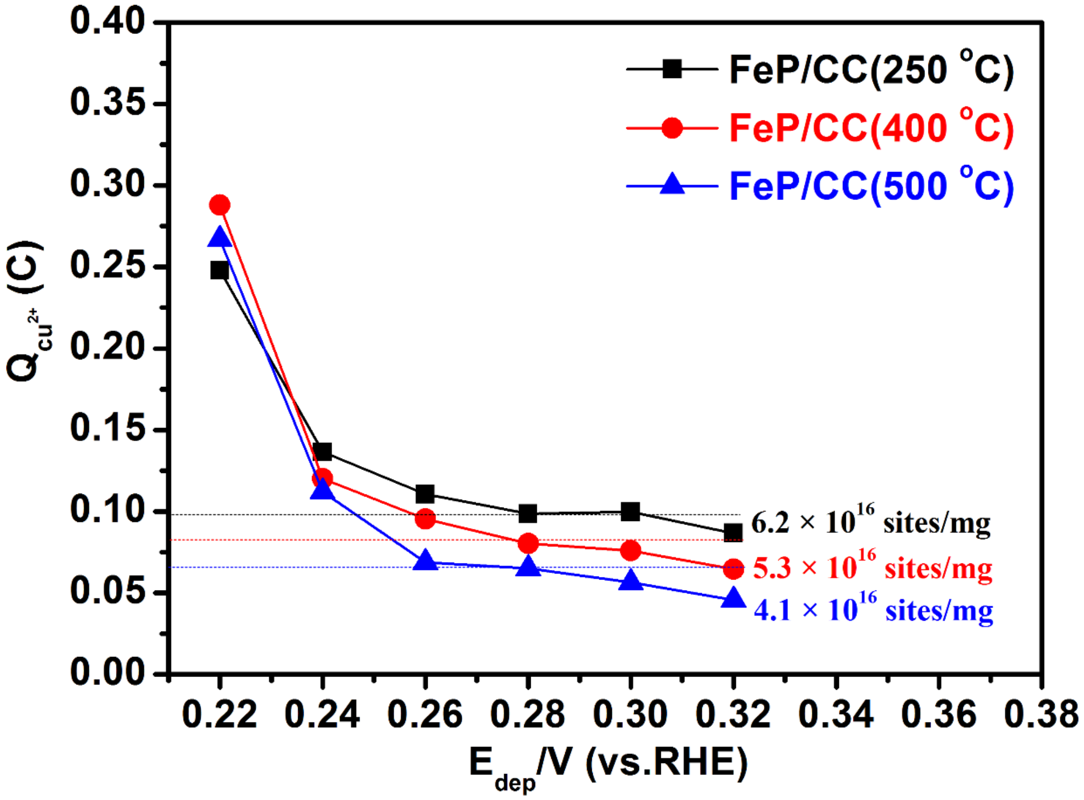

**Fig. S7** The charges required to strip the Cu deposited at different under potentials on different temperature phosphating catalysts.

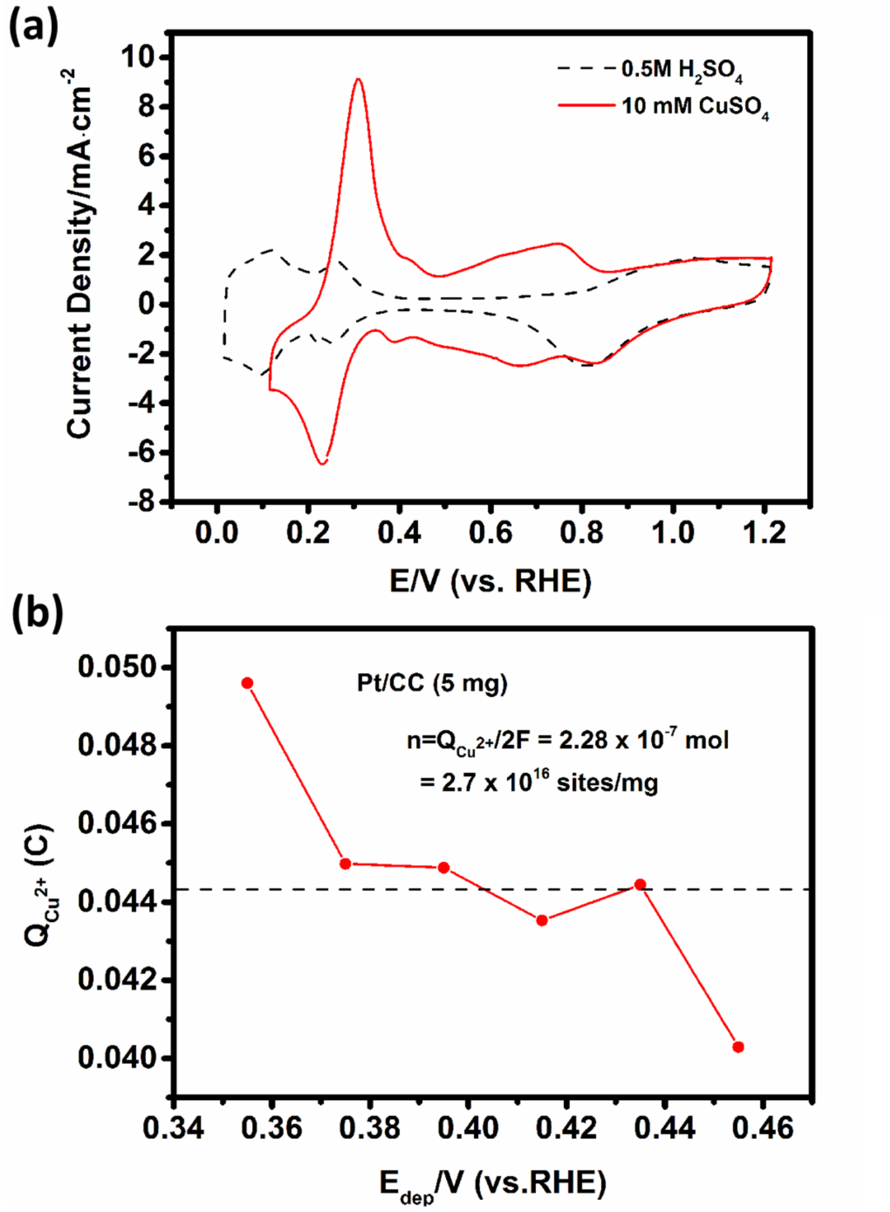

**Fig. S8** (a) The current–voltage scan for the 5mg Pt/CC catalyst (Scan procedure: from positive to negative and then positive voltages). The electrochemical processes UPD, OPD, OPD-stripping and UPD-stripping are observed in sequence. (b) The charges required to strip the Cu deposited at different underpotentials.

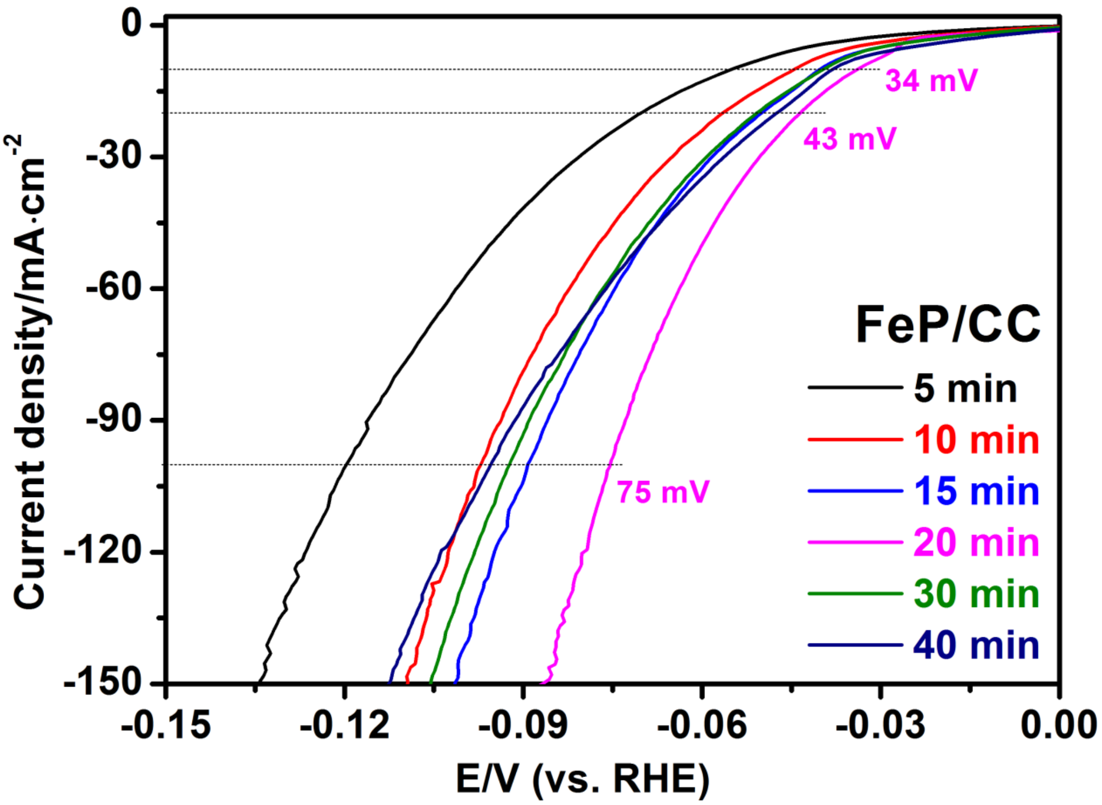

**Fig. S9** Polarization curves of the FeP/CC with different electrochemical deposition times, where the current is normalized by the geometrical area of carbon cloth and the potential is after internal resistance correction.

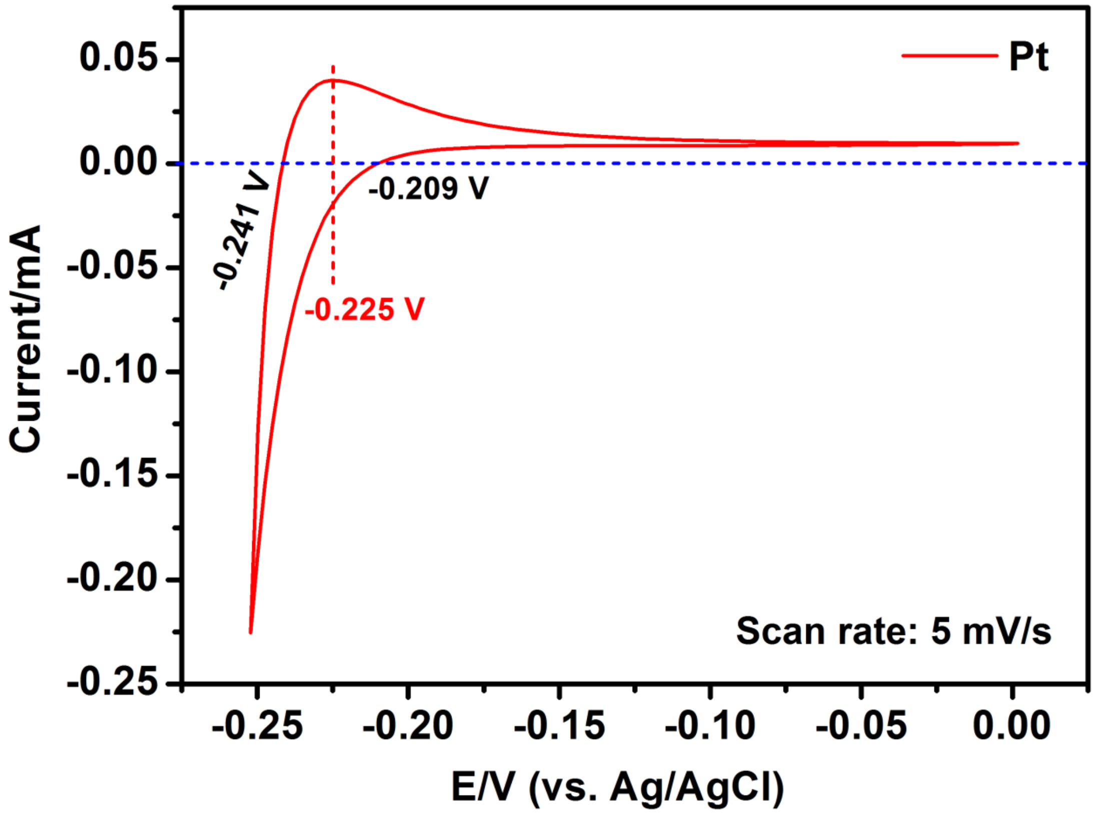

**Fig. S10** The RHE calibration was performed in the high purity hydrogen saturated electrolyte with a Pt wire as the working electrode. The current-voltage scans were run at a scan rate of 5 mV·s$^{-1}$, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. Our result shows that the E(Ag/AgCl) is lower than E(RHE) by 0.225 V. This value is consistent with the value 0.228 V from Nernst equation as described in experimental section.