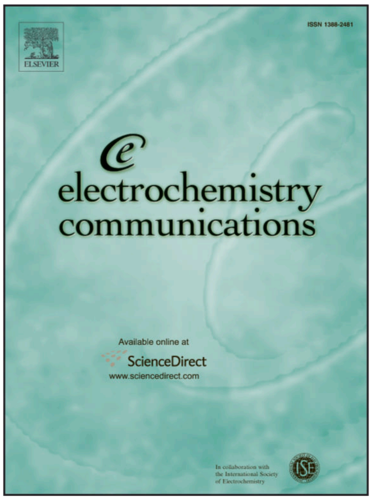

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Tailoring the Electrochemical Hydrogen Evolution Activity of Cu_3P through Oxophilic Surface Modification

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Abstract

The hydrogen evolution reaction in alkaline medium can be promoted by the modification of platinum group metal with oxophilic metals. Herein, an earth abundant metal was first converted to copper phosphide Cu_3P and the latter was electrochemically activated by a short and simple procedure to yield an oxidized electroactive surface. Compared with the pristine Cu_3P catalyst, the electrochemical activated Cu_3P catalyst exhibits an HER overpotential of 155 mV at 10 mA/cm^2 (90 mV decrease from Cu_3P catalyst) in alkaline medium with a stability over 24 hours). XRD, XPS and EDS reveal that the oxidation occurs only on the surface of Cu_3P which shows the presence of both copper phosphide and oxide species.

1. Introduction

Hydrogen evolution reaction (HER) is a reaction of technological significance as it enables the production of hydrogen, a clean energy carrier, from a water-splitting process using electrical energy.[1,5] Platinum (Pt) is considered to be the benchmarked electrocatalyst for HER because of its strong ability for the adsorption and recombination of reactive hydrogen intermediates.[3] In case of Pt, the HER activity in alkaline medium is much weaker than in an acidic electrolyte,[4,5] However, the HER activity of Pt in alkaline medium can be enhanced with a bifunctional Pt-

$Ni(OH)_2$ composite.[6] Such an effect has been shown, with hybrid catalysts featuring a single layer of $Ni(OH)_2$ nanosheets on Pt[7] or an arrangement of nanometer-scale $Ni(OH)_2$ clusters on Pt[8] demonstrating an enhanced HER activity in alkaline media compared to the standard Pt/C catalyst. The activity of nickel, silver, and copper catalysts for the HER in alkaline solutions were also enhanced by modification of the metal surfaces with $Ni(OH)_2$.[9] This demonstrates that oxophilicity is an efficient handle for promoting HER catalysis in alkaline conditions.

The HER performance of a series of Cu−M bimetallics[10] and Cu- Metal oxides or hydroxides catalysts were studied, revealing that the modification of Cu surface with oxophilic metals/metal hydroxides improved the HER activity of pure Cu. In case of Cu the adsorption of water molecule through the interaction of the proton group and eventual formation of H_{ads} is rather difficult because of its weak hydrogen binding sites. However, with the addition of an oxophilic site such as hydroxides/oxides can help adsorb water to the surface through weak interactions with the oxygen atom of the hydroxyl group while a nearby Cu site can facilitate the formation of H_{ads} . [11] .Even though such a chemical treatment important, too high coverage leads to a decrease in performance due to the passivation of the Cu active sites Nevertheless, metallic copper is not a good catalyst for HER and this study is having only fundamental interest. Recent studies have demonstrated the enhanced HER activity of earth-abundant metal phosphides, which still have to be rationalized except for some hydrogen binding calculations with more knowledge on the nature of their surface chemistry. Among the various catalysts studied the phosphides of Ni, Co, Cu and Fe got tremendous attraction due to its low cost and high performance.[12–14] Here in, we propose that the HER performance of Cu_3P (an active catalyst for HER) could further be improved with the assistance of copper oxide/hydroxide species through a simple electrochemical route. Cu hydroxide materials have previously not been associated with HER activity but the change in oxophilicity of the Cu_3P catalyst should give an improved HER performance on the hybrid surface.

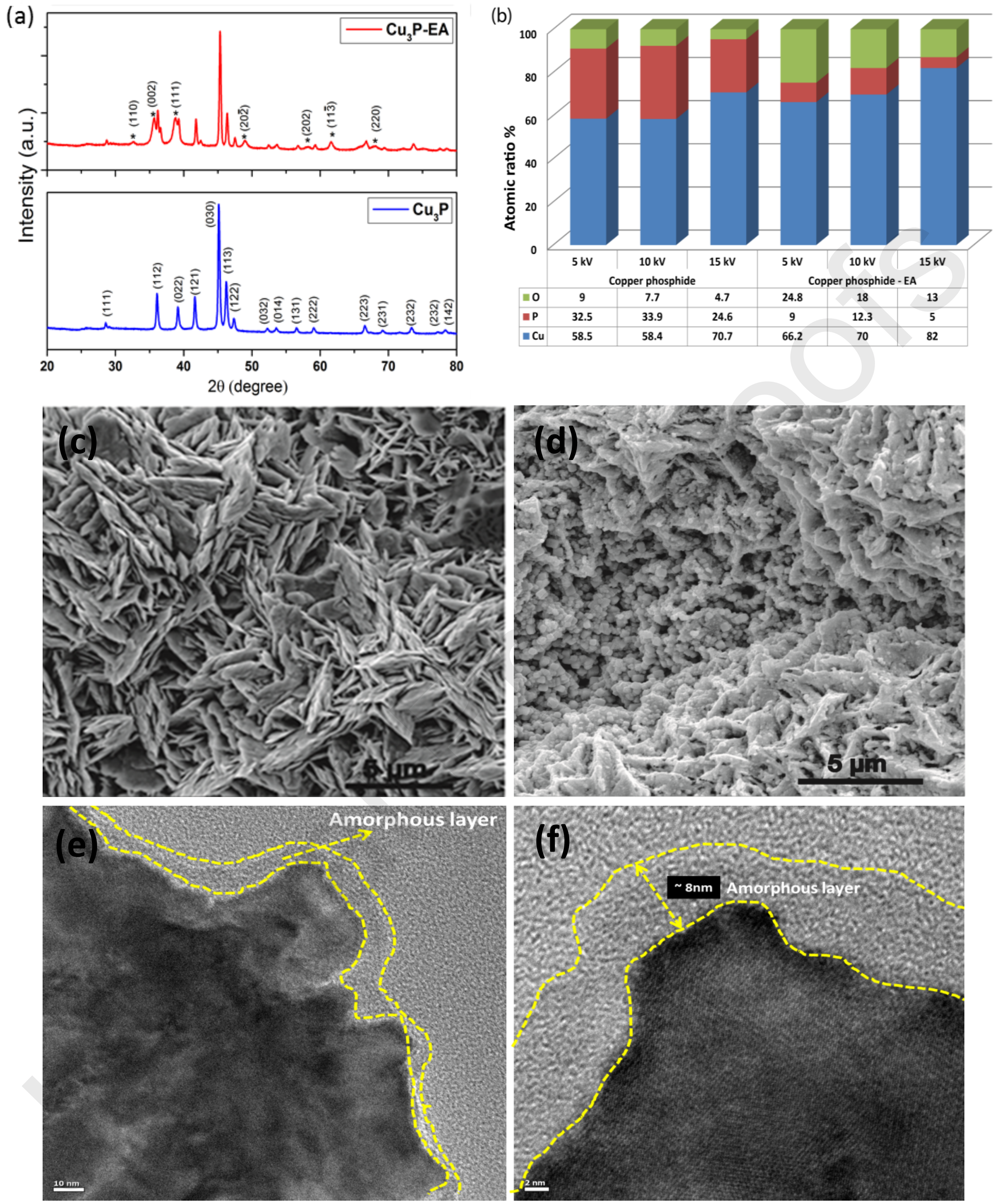
2. Materials and Methods

Copper phosphide (Cu_3P) was synthesized in a two-zone furnace by vapor transport. A Cu mesh (Nano-Nouvelle, Australia) was located in the cold zone of a quartz tube and a boat of 18 mg red phosphorus (Sigma Aldrich, 97%) was placed in the hot zone. The system was placed under vacuum and the cold and hot zones were respectively set to 160°C and 430 °C. The reaction was continued for 30 min to obtain the final product Cu_3P. The crystalline phases of the pristine copper membrane, freshly prepared Cu_3P and electrochemical activated Cu_3P materials were examined by X-ray diffraction (XRD, Bruker D8 advance). The morphology and elemental compositions of copper phosphide catalysts reported in this work were visualized using scanning electron microscopy (SEM, FEI Magellan 400) equipped with an energy-dispersive X-ray spectroscopy attachment. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa) was used to analyze the surface composition of the copper phosphide membrane before and after electrochemical activation.

Linear sweep voltammetry (LSV) measurements were conducted in 0.1 M KOH aqueous solution for the HER before and after electrochemical activation with a sweep rate of 5 mV s^{-1}, with a Bio-Logic VMP3 potentiostat. All polarization curves were corrected by current-resistance (iR) compensation within the cell. All the experiments were carried out using Milli Q water (18.2 MΩ cm^{-1}) at room temperature. The electrochemical impedance spectroscopy (EIS) was tested by using an alternating current voltage of 10 mV in the frequency range of 10 mHz to 100 kHz. The long-term stability test was performed using chronoamperometry with overpotential of 0.2 V. Double layer capacitance measurements were done on both the electrodes from 0.1V to 0.3V. The fresh prepared electrode was tested as hydrogen evolution reaction catalyst in a 0.1M KOH solution. The electrochemical activity of the as prepared samples was evaluated in a Teflon three electrode cell from, which consists of Cu_3P as working electrode, glassy carbon and Hg/HgO as counter and reference electrode respectively. All the reference electrode potentials were converted to RHE using Nernst equation unless otherwise stated. After the first linear sweep voltammetry (LSV) in the HER region, the electrode was activated at 1.7 V for 2.5 hours in the same solution. This step was named electrochemical activation (EA) of the catalyst and the sample named Cu_3P-EA. After the activation step, the HER activity was measured again.

3. Results and Discussion

The phosphorous vapor transport process yielded a black mesh (named Cu_3P) as we mentioned in previous report[15]. The sample was electrochemically activated for 2 hours at 1.7 V in 0.1M of KOH solution, to yield electrochemically activated copper phosphide (Cu_3P-EA). During this process, the surface of copper phosphide was oxidized to copper oxides/hydroxides. The material characterization by X-ray diffraction analysis was done on the three samples: starting material of copper membrane, Cu_3P and Cu_3P-EA. The diffraction pattern of Cu_3P (Fig. 1a) shows the characteristic peaks of hexagonal Cu_3P (JCPDS 071-2261) within the space group P63cm. The diffraction peaks of metallic Cu were not detected, as evidenced from the comparison of the Cu_3P diffraction pattern to the Cu pattern (Fig. 1a), which confirms the complete conversion to Cu_3P. XRD analysis of Cu_3P electrode after electrochemical activation (Cu_3P-EA) showed diffraction peaks of the hexagonal Cu_3P (JCPDS 071-2261) along with Copper oxide (CuO, monoclinic (tenorite), space group C12/c1). The XRD results clearly confirm that the electrochemical activation resulted in the oxide formation on top of Cu_3P ((Fig. 1a).



	Copper phosphide 5 kV	Copper phosphide 10 kV	Copper phosphide 15 kV	Copper phosphide - EA 5 kV	Copper phosphide - EA 10 kV	Copper phosphide - EA 15 kV
🟩 O	9	7.7	4.7	24.8	18	13
🟥 P	32.5	33.9	24.6	9	12.3	5
🟦 Cu	58.5	58.4	70.7	66.2	70	82

Figure 1. (a) XRD analysis of Cu_3P as prepared – blue curve and Cu_3P-EA – red curve (* indicates the phase corresponds to CuO) (b) EDS results of Cu_3P and Cu_3P–EA at three operating voltages – 5, 10 and 15 kV. (c-d) SEM images of Cu_3P and Cu_3P-EA (e-f) TEM and HRTEM images of Cu_3P-EA.

The EDS analysis (Fig. 1b) reveals that the Cu_3P is composed of Cu and P elements in the along with oxygen. Oxygen atoms are detected mainly on the surface while the composition is close to stoichiometric Cu_3P in the bulk of the sample. The amount of oxygen is low in Cu_3P, even close to the surface (9% atomic ratio at 5kV). EDS analysis of Cu_3P-EA shows an increase in oxygen content for all operating voltage values, especially on the surface (24.8 % atomic ratio at 5kV). The morphology of Cu, Cu_3P and Cu_3P-EA are revealed using SEM. The surface of Cu_3P is evenly covered by plaques formed perpendicular to the surface (Fig. 1c). After electrochemical activation, the SEM micrographs reveal the same plaques, but with more surface roughness due to the bubble formation during the activation process (Fig. 1d). After electrochemical activation of Cu_3P, we expect the formation of oxide/hydroxide species on the surface of the electrode. The thickness of the amorphous layer formed on the surface of Cu_3P is found to be 8 nm using TEM and HRTEM analysis (Fig. 1e and Fig. 1f). The amorphous layer is conformal on all the flakes observed by HRTEM.

For detailed characterization of the chemical composition on the Cu_3P-EA, we analyzed and compared the XPS spectra of Cu_3P-EA and in-situ ion-etched Cu_3P-EA to gain knowledge on the chemical nature of the Cu_3P surface and sublayer after electrochemical activation. Fig. 2 shows high-resolution Cu 2p and P 2p XPS spectra of the Cu_3P-EA before and after the etching. As shown in Fig.2a before and after etching, the Cu_3P-EA displays two major peaks corresponding to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ at respectively 932.8 eV and 952.6 eV. The binding energy values of 933.7 eV, 934.9 eV and 954.1eV correspond to the oxidized copper at the surface of Cu_3P. After the etching process the percentage of oxidized copper at the surface of Cu_3P-EA is drastically reduced as shown in Fig. 2c. The deconvoluted P 2p spectrum of Cu_3P- EA before etching shows binding energy values only above 131 eV, which indicates that the phosphide ion present on the surface of Cu_3P- EA is also oxidized during the electrochemical activation process. After etching the P_2P spectra of Cu_3P- EA shows a new set of peaks centered at 129.3eV and 130.1 eV, which corresponds to $2p_{3/2}$ and $2p_{1/2}$ of unoxidized phosphorous respectively. The results clearly confirm that only the surface of Cu_3P is converted to an oxide or a hydroxide during the electrochemical activation.

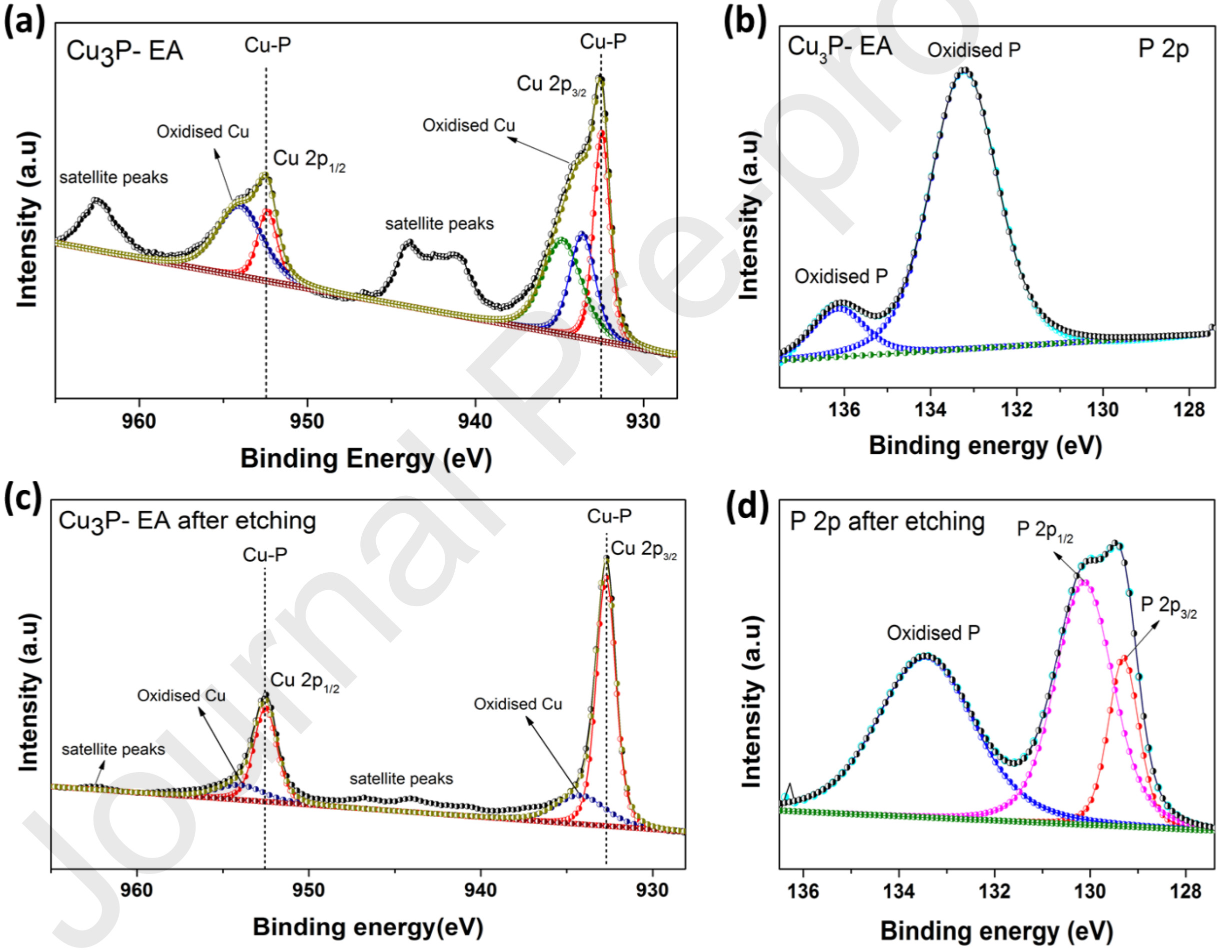


Figure 2: High resolution XPS spectra of (a) Cu 2p and (b) P 2p in Cu_3P-EA before etching. High-resolution XPS spectra of (a) Cu 2p and (b) P 2p in Cu_3P-EA after etching.

In order to evaluate the hydrogen evolution reaction (HER) activity of the catalysts, the linear sweep voltammetry (LSV) in alkaline conditions was collected for pristine Cu membrane, activated Cu membrane (Cu-EA), Cu_3P and Cu_3P-EA (Fig. 3a). The pristine Cu membrane displays a high overpotential (> 600 mV), even after electrochemical activation. The overpotentials measured at a current density of 10 $mAcm^{-2}$ for Cu_3P and Cu_3P-EA are respectively 250 mV and 155 mV. The result clearly indicates that the electrochemical oxidation at 1.7 V nets a gain of 95 mV at a current density of 10 mA/cm^2. The overpotential to reach a current density of 10 $mAcm^{-2}$ is 50 mV for commercial Pt/C and the values are very close to other reported recently reported Cu_3P systems [16–20]. The overpotential reaches a plateau after only 30 minutes of electrochemical activation. The Tafel plot for the corresponding LSV measurements is shown in Fig. 3b. The Tafel slope decreases from 133 mV/dec to 125 mV/dec after electrochemical activation. Ideally, the Tafel slopes should be derived from steady-state measurements. For that purpose, the data extracted from the LSV measurements at 5 mVs-1 was double-checked with chronoamperometric measurements. Fig. 3c shows the EIS spectra of the electrodes under HER conditions. Among the two electrodes, Cu_3P-EA shows the lower charge transfer resistance value (7.5 Ω) in comparison to its Cu_3P counterpart (10.5 Ω), which indicates the faster electron transfer kinetics of Cu_3P-EA in alkaline HER conditions. The stability of Cu_3P-EA electrode towards HER was performed at an over potential of 160 mV and 200 mV (Fig. 3d and Fig. 3e). In both cases, the current density was found to be stable for more than 24 hours. The material is found to be leaching out from the surface at higher current density (100 $mAcm^{-2}$). In order to stabilize the membrane, we coated nafion on the surface of Cu_3P-EA and performed the stability test and the material was found to be stable for more than 12 hours as shown in Fig. 3f.

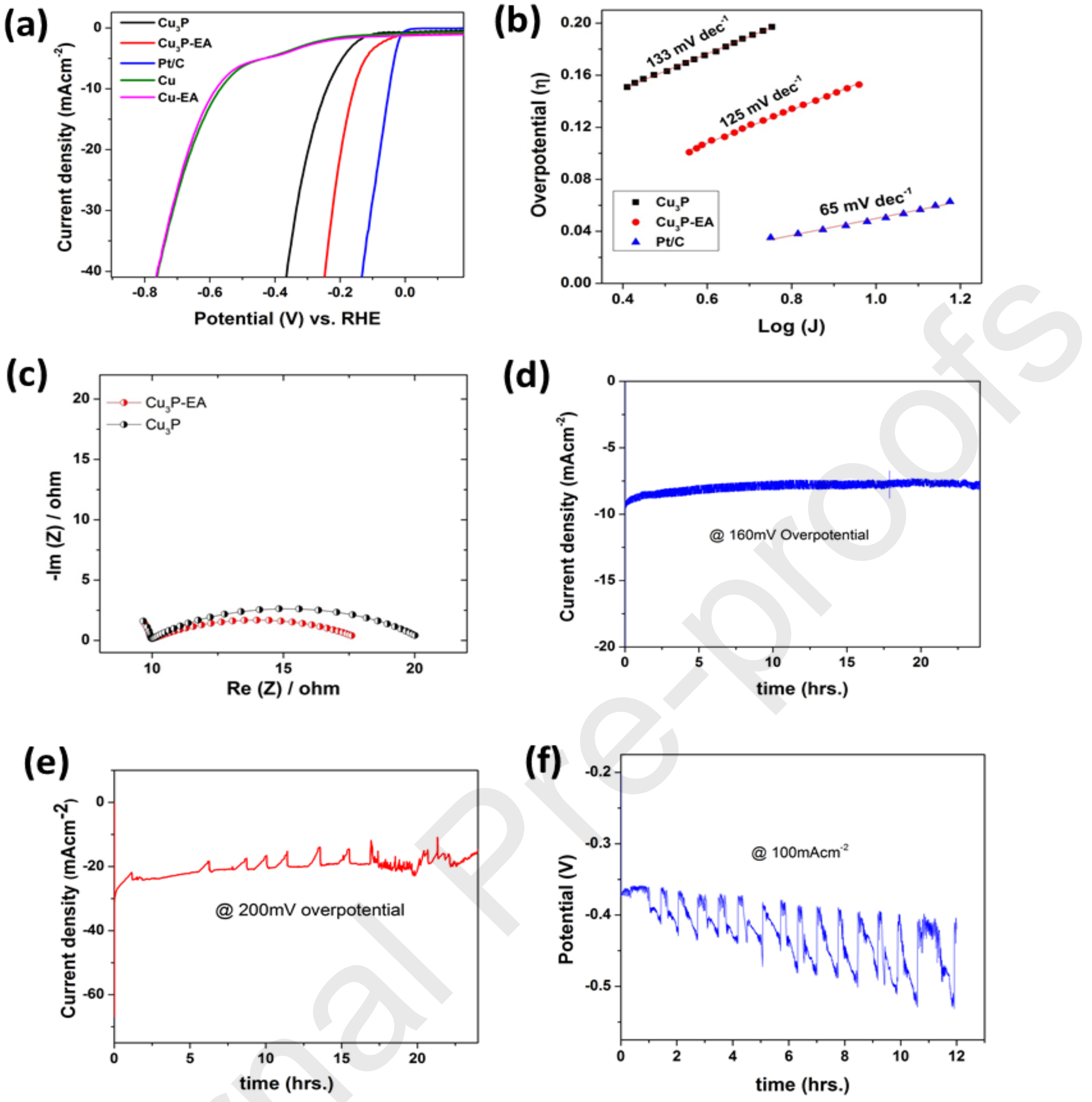


Figure 3: (a) LSV polarization curves of different materials, (b) Tafel plots of Cu_3P ,Cu_3P-EA Nd Pt/C (c) Nyquist plots of EIS of Cu_3P and EA-Cu_3P samples in 0.1 M KOH at an applied over potential of 100 mV vs. RHE , (d & e) chronoamperometric measurement at 160 mV and 200 mV overpotential, (f) chronopotentiometric measurement at 100 mAcm^{-2}.

The electrochemical surface area (ECSA) can be used as an approximate guide for surface roughness within an order-of-magnitude accuracy. To estimate the effective surface areas of Cu_3P and Cu_3P-EA, we measured the capacitances of the double layer at the solid/liquid interface. The cyclic voltammograms (CVs) were collected in the region of 0.10–0.30 V with scan rate varying from 10 mV/s to 60 mV/s, where the current response should only be due to the charging of the double layer (Fig. 4). The capacitances of Cu_3P and Cu_3P-EA are respectively 22.5 and 25.5 mF/cm^2, thus indicating that the electrodes have a similar surface roughness. Therefore, we can conclude that the increased HER activity of the Cu_3P-EA is solely due to the oxides/hydroxides formation and not to the increased ECSA of the Cu_3P formed at high potentials by bubbling.

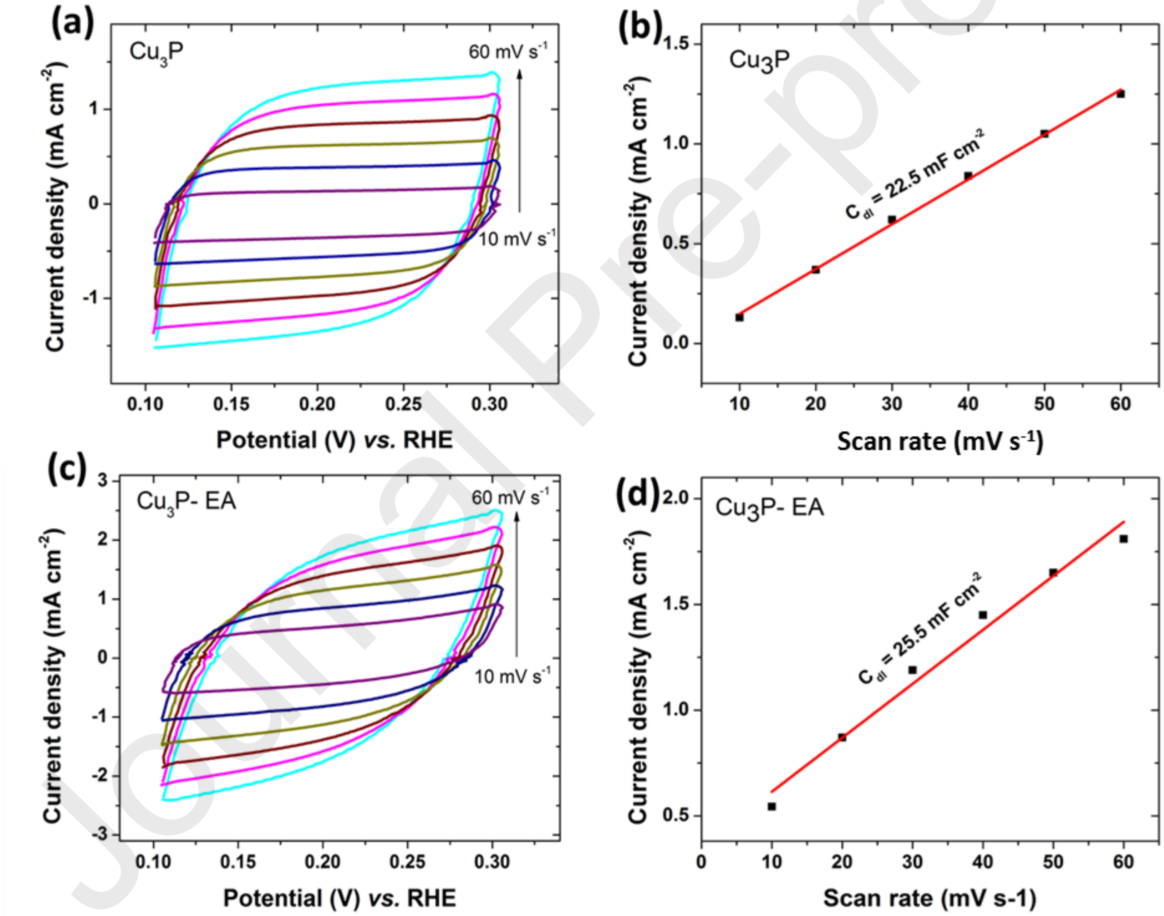


Figure 4: (a) CV in 0.1 M KOH solution and (b) corresponding capacitive currents at 0.20 V as a function of scan rate for Cu_3P; **(**a) CV in 0.1 M KOH solution and (b) corresponding capacitive currents at 0.20 V as a function of scan rate for Cu_3P-EA.

The surface characterization of the oxidized catalyst by XPS and HRTEM, which consists of a layer of oxide origin, provides some hints about the origin of the enhanced HER activity. This oxide layer of a few nanometers is interfaced with the Cu_3P underlayer. In our controlled experiment on the Cu membrane, we found that metallic Cu is a poor HER catalyst, even after surface oxidation. Therefore, the Cu_3P/CuO interface seems to be instrumental to promote the HER activity. Moreover, the sample did not show any change after the stability test as shown in the SEM images (Fig. 5a and 5b).

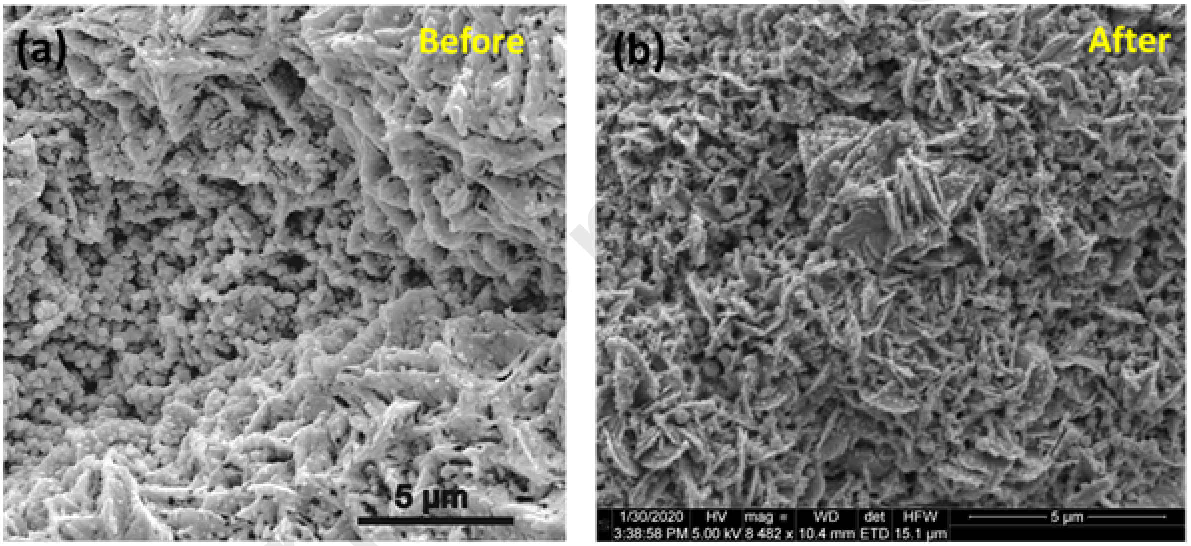


Figure 5: (a) SEM images of Cu_3P-EA before (a) and after (b) the stability test

3. Conclusion

Cu_3P was synthesized by vapor transport from a Cu mesh and the Cu_3P surface was partially oxidized through a simple method of electrochemical activation. Compared with the pristine Cu_3P catalyst, the electrochemical activated Cu_3P-EA catalyst exhibits an HER overpotential of 160 mV at 10 mA/cm^2 (90 mV decrease from Cu_3P catalyst) in alkaline medium with a stability over 24 hours. The ECSA estimated from the double layer capacitance measurements show similar values for the catalyst before and after electrochemical activation. The enhanced HER catalytic activity is therefore attributed to the partial coverage of Cu_3P with oxophilic species – copper and phosphorous oxide/hydroxide on the surface. XRD, XPS and EDS reveal that the oxidation occurs only on the surface of Cu_3P-EA which shows the presence of both copper phosphide and oxide species. Further we would like to extend our study using laser-induced temperature jump technique to explain the mechanism of enhanced activity after activation.

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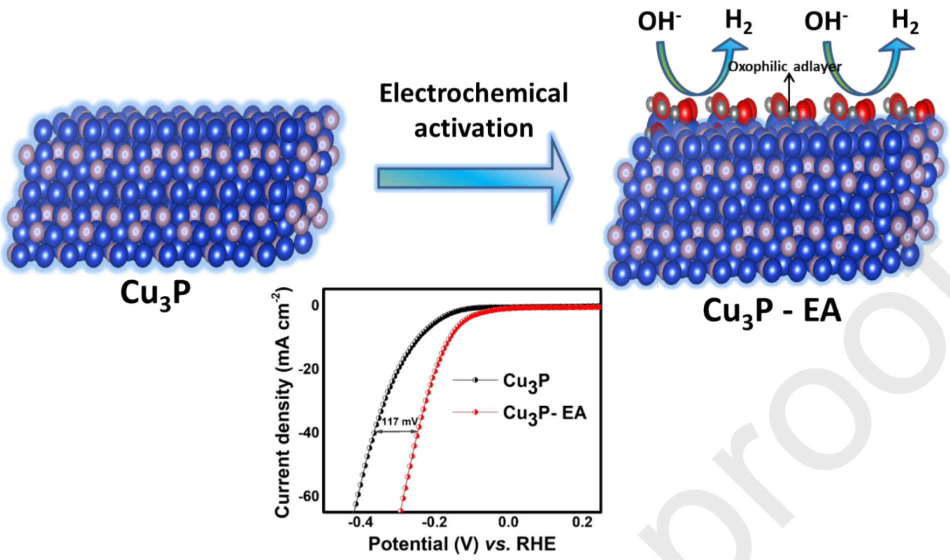
Graphical abstract



Thazhe Veettil Vineesh: conceptualization, methodology of the electrochemical study, Writing - Original Draft, visualization. **Valeria Yarmiayev**: investigation of the synthesis. **David Zitoun**: supervision and Writing - Review & Editing

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

1. Electrochemically activated Copper Phosphide (Cu_3P) demonstrates an overvoltage of only 160 mV at a current density of 10 mAcm-2 for hydrogen evolution activity in alkaline medium with stable activity over 24 hours.

2. The surface oxophilicity of Cu_3P is tuned through a simple electrochemical oxidation and the materials were thoroughly characterised by various electrochemical, microscopic and spectroscopic methods.

3. The electrochemically activated Copper phosphide (Cu_3P-EA) showed improved performance in comparison with the pristine Cu_3P counterpart.

4. A net gain of 90mV was obtained at a current density of 10 $mAcm^{-2}$, opens a new avenue to further improve the HER activity of metal phosphides.