Supporting Information

Genomic DNA mediated formation of porous 
\(\text{Cu}_2(\text{OH})\text{PO}_4/\text{Co}_3(\text{PO}_4)_2.8\text{H}_2\text{O} \) rolling pin shape bifunctional 
electrocatalyst for water splitting reactions

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Instrumentations:

Powder X-ray diffraction (PXRD) pattern was obtained on a Bruker D8 Advances instrument using Cu-Kα (λ = 1.5406 Å) radiation in the 2θ range from 10° to 80° with an acceleration voltage of 40KV. ATR-FTIR were performed using Bruker (Model: Vertex 70v) ATR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using the Thermo Scientific Inc. System equipped with a microfocus monochromatic Al Kα X-ray source of energy ~1450 eV. All electrochemical measurements were performed with Metrohm Autolab (M204 multichannel potentiostat galvanostat using Nova 2.1.4 software. Transmission electron microscope (TEM) images were taken using JEOL, JEM-2100F at an operating voltage of 200 kV. ICP-MS was carried out by Thermo Scientific (Model no. ICAPQ). Brunauer-Emmett-Teller (BET) measurement was carried out with Make-Quanta Chrome instruments, Model: AutosorbiQ and ASiQwin UV-1601 spectrophotometer (SHIMADZU), Great Multiuser Thermal Cycler (Applied Biosystem).

Synthesis Method and Experimental Section:

Materials used: Copper(II) acetate monohydrate 99% (Cu(OCOCH₃)₂·H₂O), Cobalt(II) chloride hexahydrate 98% (CoCl₂·6H₂O), Potassium dihydrogen phosphate (KH₂PO₄) were purchased from the Loba Chemie India, and material used for DNA extraction are Chloroform & agarose gel (Amresco) isoamyl alcohol (SDFCL) TE buffer, Ethidium bromide solution & RNase A (Himidia), sodium acetate (Sigma) PCR buffer, dNTPs & Taq DNA (Applied Biosystem, Foster City, CA, USA ) 25 mM MgCl₂ (Merk) and 10mM primer (Imperial Life science India) All chemicals are stored in dry place and used without further purification.

Extraction Protocol of DNA:

DNA was isolated by using following protocol (Dolye, 1990)

About 5 gm plant tissues were grinded using liquid nitrogen in pre chilled mortar and pestle and grinded plant material was then transferred to 25 ml centrifuge tube containing 10ml pre warmed extraction buffer. Mix by inversion and incubate at 60 °C for 1 hr. The suspension was cooled down at room temperature for 5 minutes and 10 ml of chloroform-isoamyl alcohol (24:1) was added and mix by inversion for 10 mins followed by centrifugation at 12000 rpm for 20 minutes at room temperature. Supernatant was transferred to fresh centrifuge tubes using a wide bore pipette tip. Then, 2/3rd volume of isopropanol alcohol was added and mixed by gentle inversion. Centrifuged at 10,000 rpm for 10 min. Further, the supernatant was discarded and DNA pellet was washed twice with 3ml of 70% alcohol and was dried overnight at room temperature. Later to dissolve the dried pellet, 3 mL of TE buffer was added and stored at 20°C.

For the purification of extracted DNA is required to remove the contaminants such as RNA, proteins and polysaccharides. RNA contamination is removed by the treatment of RNase A while proteins are removed by phenol: chloroform treatment. Following protocol was used to purify DNA: to 3ml of DNA sample added 30 μL of DNA-free RNase A (10 μ/μL) and incubated at 37°C for 1 h. Further, to above solution (3ml) equal volume of phenol-chloroform-isoamyl alcohol (25:24:1) was added, mix by gentle inversion for 5-10 min, and centrifuged for 10 min at 10000 rpm at room temperature, top aqueous layer was taken into a new 10-ml centrifuge tube and were mixed with 1/10th volume of 3M sodium acetate and two volumes of absolute alcohol and centrifuged at 13,000 rpm for 3 min. Further, the supernatant was discarded and DNA pellet was washed twice with 3ml of 70% alcohol and dried overnight. The dried DNA pellet was dissolved in TE buffer.
Dry it and add 1 mL TE buffer to dissolve the pellet. Moreover, dilute 15 μL of DNA solution to qualitative assay with a UV-1601 spectrophotometer (SHIMADZU) and adjust the concentration of the samples to 200 ng/μL to add 5 μL of each sample to test on a 0.8% agarose gel. Store the DNA solution at -20°C until use. Isolated genomic DNA was amplified by using reaction mixtures of 20 μL containing 10X PCR buffer, 25 mM MgCl₂, 10mM dNTPs, 10mM primer, Taq DNA polymerase, template DNA and autoclaved water. Primers used for amplifying the nuclear region were (White et al. 1990). Amplified products and a standard 100 bp DNA marker were electrophoresed on 1 % agarose gels for 45min at 90V and visualized under Ethidium Bromide to determine the approximate length and purity (citation).

Complete DNA Sequence:

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1  ggtatcctgcc  agatgtcagt  atgaactatt  cagattgtga  aactgcgaat  ggctcattaa
61  atcagttata  gtgtttagta  tgtgatctgc  tctcgtgata  cagttagtga  acgcctgccgt
121  aaaaccccgg  ccctagctgc  ttgcgtcagc  ccgcttctgc  ccccttctgc  tgtgatctgc
181  cggcttcgct  ccctctggaa  gggatgcatt  tattagaaaa  aaggtcaatg  cgggcttctg
241  ggtgtctca  ccatcactaa  cttagctgata  ttagttttaga  tattacattc  ccaccgctttg
301  acgcttctgc  tcataatcctt  ggttgtttaga  tgtgatctgc  ccccttctgc  tgtgatctgc
361  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc  tgtgatctgc
421  agtgcggcgc  gctgtcttttt  ggttgtttaga  tgtgatctgc  ccccttctgc  tgtgatctgc
481  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
541  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
601  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc  tgtgatctgc
661  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc  tgtgatctgc
721  agtgcggcgc  gctgtcttttt  ggttgtttaga  tgtgatctgc  ccccttctgc  tgtgatctgc
781  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
841  atttctgta  catttcttggc  tgtgatctgc  ccccttctgc  tgtgatctgc  ccccttctgc
901  aaaaaaaa  aaagatggtc  acggccggcc  ggtgtctca  atatattata  gtaattcttgc
961  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1021  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1081  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1141  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1201  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1261  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1321  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1381  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1441  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1501  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1561  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1621  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
1681  cctccggttt  ggtgtctca  atatattata  gtaattcttgc  tgtgatctgc  ccccttctgc
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Synthesised Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite structures:

Synthesis of nanocomposites were carried out at room temperature and in aqueous medium. Copper acetate (0.5 m mol) and cobalt chloride (0.75 m mol) was dissolved in 10 ml of water under magnetic stirrer at 1000 rpm. Then 0.75 m mol KH$_2$PO$_4$ was dissolved in 10 ml water in another beaker separately. Next, the DNA solution (50 µl DNA was dissolved into 1 ml DI H$_2$O) was added drop wise in the metal ions solution. After 10 min, prepared KH$_2$PO$_4$ solution was added to the above reaction mixture under stirring condition. After 2 hours, the reaction mixture was centrifuged at 4000 rpm and washed 3 times with DI water. The obtained product was dried in oven at 50ºC for 1 day.

Synthesised Co$_3$(PO$_4$)$_2$.8H$_2$O structures:

Co$_3$(PO$_4$)$_2$.8H$_2$O was synthesised following by the above method in absence of copper acetate under same reaction conditions.

Synthesised Cu$_2$(OH)PO$_4$ structures:

Cu$_2$(OH)PO$_4$ was synthesised following by the above method in absence of cobalt chloride under same reaction conditions.

Preparation of working electrode and electrochemical experiments:

Preparation of catalyst inks were done by dissolving 4 mg of the catalyst in a mixture of 300 µL of double distilled (DDI) water and 200 µL ethanol and the solution were kept in a 1.5 mL micro centrifuge tube for Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O material, whereas for Cu$_2$(OH)PO$_4$/ Co$_3$(PO$_4$)$_2$.8H$_2$O with binder, same procedure of preparation was followed but here we use 10 µL Nafion (Sigma-Aldrich) solution followed by sonication of another 15 min which act as a binder. In both case, the as-prepared 5 µL catalyst ink was drop casted on to the glassy carbon (GC) electrode and left overnight in vacuum desiccator for drying. The dried electrode is used as working electrode (WE) for the study of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) activity.

All the electrochemical measurements were carried out at room temperature using Metrohm Autolab (Multichannel-204) connected to a standard three-electrode system using Nova 2.1.4 software. For the electrochemical measurements, here, a conventional three-electrode system was used where Ag/AgCl (3 M KCl) and platinum (Pt) electrode were act as reference and counter electrode for OER and Ag/AgCl (3 M KCl) and graphite electrode were act as reference and counter electrode, respectively. Whereas the GC (Glassy Carbon) act as a working electrode. Before all the electrochemical measurements, the electrolyte solutions (1 M KOH and 0.5 M H$_2$SO$_4$) were prepared with double distilled water (18.2 Milli-Q) and degassed by purging of bubbling nitrogen gas for 30 min at room temperature. All the experiments related to OER and HER were performed out in 1 M KOH (pH = 13.8) and 0.5 M H$_2$SO$_4$ solution prepared using double distilled water, respectively.

Additionally, the electrochemically active surface area (ECSA) is proportional to the electrochemical double layer capacitance ($C_D$), can be calculated using the equation:

$$\text{ECSA} = \frac{C_{dl}}{C_s}$$

Where $C_s$ is the specific capacitance of flat working electrode with actual surface area of 1 cm$^2$ and taken its value is 40 µF·cm$^{-2}$ per cm$^2$ for the flat electrode. From ECSA calculations, it was found the Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite has higher electrochemically active area, than that of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O with external binder (nafion), Co$_3$(PO$_4$)$_2$ and Cu$_2$(OH)PO$_4$ nanostructures. The electrochemically active surface area (ECSA) has another a noteworthy factor that has an impact on the OER activity of the nanostructures. The electrochemical double layer capacitance measurement of as
synthesized nanostructures was carried out by CV plot at different scan rates, which are shown in Figure S1. Additionally, from slope measurements, it is observed that the Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$·8H$_2$O composites has higher electrochemical double layer capacitance ($C_d$) of 4.7 mF cm$^{-2}$, than that of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$·8H$_2$O with external binder (3.945 mF cm$^{-2}$), Co$_3$(PO$_4$)$_2$·8H$_2$O (1.73 mF cm$^{-2}$), Cu$_2$(OH)PO$_4$ (1.28 mF cm$^{-2}$) and their corresponding ECSA was calculated to be 117.5 cm$^2$, 98.6 cm$^2$ (with binder), 43.2 cm$^2$ and 32.1 cm$^2$, respectively.

Figure S1. Cyclic voltammetry curves of (a) Cu$_2$(OH)PO$_4$/ Co$_3$(PO$_4$)$_2$·8H$_2$O, (b) Cu$_2$(OH)PO$_4$/ Co$_3$(PO$_4$)$_2$·8H$_2$O with binder, (c) Co$_3$(PO$_4$)$_2$·8H$_2$O, (d) Cu$_2$(OH)PO$_4$ and (e-h) are their corresponding plot of cathodic current ($I_c$) and anodic ($I_a$) against scan rate for the determination of double layer capacitance ($C_d$) of the catalysts, respectively.

Figure S2. XRD patterns of as synthesised (a) Cu$_2$(OH)PO$_4$, (b) Co$_3$(PO$_4$)$_2$·8H$_2$O.
Figure S3. Elemental mapping of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite: (a) Cu, (b) Co, (c) O, (d) P, (e) C, (f) N elements.

Figure S4. FE-SEM of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite synthesised in the absence of DNA.
Figure S5. (a, b) FE-SEM and (c, d) TEM images of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O catalyst before and after catalytic activity (after chronoamperometry stability test), respectively, and (e) XRD pattern of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O before and after catalysis (chronoamperometry stability test).

Figure S6: BET analysis: The N$_2$ adsorption-desorption isotherm and pore size distribution of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite.

Table S1: Crystal phase details of as synthesised samples.

| Sample                        | Crystal Type   | Space Group | a (Å)   | b (Å)   | c (Å)   |
|-------------------------------|----------------|-------------|---------|---------|---------|
| Cu$_2$(OH)PO$_4$ (#ICSD-200422) | Orthorhombic  | Pnnm (58)   | 8.0626  | 8.3840  | 5.8810  |
| Co$_3$(PO$_4$)$_2$.8H$_2$O (#ICSD-065687) | Monoclinic    | C2/m (12)   | 10.0210 | 13.3310 | 4.6730  |
Table S2: New unit cell value from Rietveld refinement of prepared powdered diffraction patterns with the reference patterns Cu2(OH)PO4 (#ICSD-200422) and Co3(PO4)2.8H2O (#ICSD-065687).

| Sample                  | a (Å)  | b (Å)  | c (Å)  |
|-------------------------|--------|--------|--------|
| Cu2(OH)PO4             | 8.0799 | 8.4215 | 5.8972 |
| Co3(PO4)2.8H2O         | 10.0732| 13.4008| 4.6719 |

Table S3. Summary of electrochemical OER and HER activity of as synthesised Cu2(OH)PO4/Co3(PO4)2.8H2O, Co3(PO4)2.8H2O, Cu2(OH)PO4, commercial IrO2 and commercial Pt/C catalysts.

| Catalysts                  | Overpotential at 10 mA cm⁻² | Tafel slope (mV dec⁻¹) | Rct (Ω) (OER) | Cdl (mF cm⁻²) (OER) | ECSA (cm²) (OER) |
|----------------------------|-----------------------------|------------------------|---------------|---------------------|------------------|
|                            | OER | HER | OER | HER |                   |                  |
| Cu2(OH)PO4/Co3(PO4)2.8H2O | 234 mV | 138 mV | 62 | 74 | 11.22 | 4.7 | 117.5 |
| Cu2(OH)PO4/Co3(PO4)2.8H2O with binder | 257 mV | 178 mV | 69 | 89 | 12.96 | 3.945 | 98.6 |
| Co3(PO4)2.8H2O             | 295 mV | 256 mV | 73 | 106 | 16.43 | 1.73 | 43.2 |
| Cu2(OH)PO4                 | 531 mV | 459 mV | 129 | 158 | 22.84 | 1.28 | 32.1 |
| IrO2 (OER)                 | 354 mV | - | 79 | - | - | - |
| Pt/C (HER)                 | 32 mV | - | 41 | - | - | - |

Table S4. Elemental Composition of Cu2(OH)PO4/Co3(PO4)2.8H2O acquired from ICP-MS analysis before and after HER performance.

| System                                    | Cu (Wt %) | Co (Wt %) |
|-------------------------------------------|-----------|-----------|
| Cu2(OH)PO4/Co3(PO4)2.8H2O: before catalysis | 15.87     | 22.36     |
| Cu2(OH)PO4/Co3(PO4)2.8H2O: after catalysis | 15.13     | 21.97     |
Table S5. Comparison of OER and HER activity of Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O composite nanostructure with some reported Cobalt-based catalysts and DNA based catalyst in an alkaline medium and acidic medium.

| Catalyst | Overpotential (at 10 mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | Electrolyte used | Reference |
|----------|-----------------------------------|-----------------------------|------------------|-----------|
|          | OER | HER | OER | HER | 1M KOH | HER |
| Co$_2$P/Co$_2$N@CNF-DNA | - | - | 107.42 | - | 1M KOH | - |
| Co$_{0.65}$Se-hyd | 354 mV | - | 65 | - | 1M KOH | - |
| CoSe-DNA | 383 mV | - | 71 | - | 1M KOH | - |
| Pt@DNA without binder | - | 260 mV | 30 | - | 0.5M H$_2$SO$_4$ | 3 |
| Ag-Co(OH)$_2$ on DNA | 260 mV* | - | 50 | - | 1M KOH | - |
| Co$_3$(PO$_4$)$_2$ | 299 mV | - | 44 | - | 1M KOH | - |
| Co$_3$(PO$_4$)$_2$/PCDs | 350 mV | - | 59 | - | 0.1M KOH | - |
| Co$_3$(PO$_4$)$_2$(OH)$_4$ | 254 mV | - | 57 | - | 1M KOH | - |
| NiFe-PO$_4$/NF | 206 mV | - | 31 | - | 1M KOH | - |
| Ni$_2$(OH)PO$_4$/Fe(OH)$_x$ | 248 mV | - | 45.4 | - | 1M KOH | - |
| NiCoFePO$_4$ NPs-C/NF | 240 mV | - | 57 | - | 1M KOH | - |
| Co$_3$(OH)$_2$(HPO$_4$)$_2$/NF | 240 mV | - | 69 | - | 1M KOH | - |
| CoPi/PF-CNTs | - | 105 mV | 32 | - | 0.5 M H$_2$SO$_4$ | 12 |
| rGO-CoP/Co$_3$P | - | 156 mV | 53.8 | - | 0.5 M H$_2$SO$_4$ | 13 |
| Cu$_2$(OH)PO$_4$/Co$_3$(PO$_4$)$_2$.8H$_2$O | 234 mV | 138 mV | 62 | 74 | 1M KOH | 0.5 M H$_2$SO$_4$ | This work |

Note: * = Overpotential at 50 mA cm$^{-2}$

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