Uniformly decorated molybdenum carbide/nitride nanostructures on biomass template for HER application

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S1. Synthesis of catalyst

S1.1. Synthesis of MoCot1, MoCot2, Mo$_2$C and Mo$_2$N

The general synthesis procedure of all the catalyst consists of two major steps:

The first step involves the synthesis of the catalyst precursor which has been described in the section given below and is the same for all the catalysts, i.e., MoCot, MoCot1, MoCot2 Mo$_2$C and Mo$_2$N. But the second step is different for corresponding catalysts:

**First Step:** For the precursor, typically a solution containing 2.5 mL ammonium hydroxide (25%) was formed by adding 0.01 mol of hexamethylenetetramine (HMT) and 0.001 mol of ammonium molybdate tetrahydrate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O into it and then stirred for 2hr at room temperature till it becomes transparent. The finely chopped cotton 1 g was dipped and soaked into the solution and the obtain cotton soaked material hydrothermal heated at 100°C for 12 h in the oven. After that, the product was vacuum dried in the oven for 6hr at 100°C to yield a greenish-white mass.

**Second step:** The calcination of the respective catalyst-precursors was carried out in such a way that it yields the desired products. The reaction parameters were manipulated in the following manner:

(a) **MoCot1:** For MoCot1 catalyst, the hold time in ammonia atmosphere was 30 minutes with a flow rate of 20 mL/min at temperature 650°C and after that raised to 750°C and held for 2.5 h in an argon atmosphere at a flow rate of 30 mL/min.

(b) **MoCot2:** For MoCot2, the hold time at 650°C was 1.5 h in ammonia atmosphere with a flow rate of 20 mL/min followed by annealing at 750°C for 2.5 h in an argon atmosphere at a flow rate of 30 mL/min.

(c) **Mo$_2$C:** The Mo$_2$C catalyst was synthesized simply by annealing the catalyst precursor at 750°C for 2.5 h in an argon atmosphere at a flow rate of 30 mL/min throughout the synthesis process.

(d) **Mo$_2$N:** The Mo$_2$N catalyst obtained by annealing the catalyst precursor at 650°C for two hours in the ammonia atmosphere with a flow rate of 20 mL/min.
Note: The heating rate in all the synthesis process was $7^0$C/min, and the post-reaction cooling was done in an argon environment with a gas flow of 30 mL/min.

S2. Rietveld analysis and refinement parameters of MoCot1 and MoCot2 catalysts.

Figure S1. Rietveld refinement of MoCot1 shows a composition of 72.57% and 27.43% of Mo$_2$C and Mo$_2$N respectively.

Figure S2. Rietveld analysis of MoCot2 catalyst shows a composition of 30.47 % and 69.53 % of Mo$_2$C and Mo$_2$N respectively.
Table (below) showing the unit cell parameters of MoCot, MoCot1 and MoCot2 and their corresponding refinement values.

| Sr. No. | Parameters | Mo$_2$C | Mo$_2$N |
|---------|------------|---------|---------|
| 1       | Symmetry   | Hexagonal | Cubic  |
| 2       | Space group| 194     | 225     |
|         | Input | Output | Input | Output |
| 3       | a     | 2.99091 Å | 3.00234 Å | 4.16158 Å | 4.15397 Å |
| 4       | b     | 2.99091 Å | 3.00234 Å | 4.16158 Å | 4.15397 Å |
| 5       | c     | 4.71022 Å | 4.74732 Å | 4.16158 Å | 4.15397 Å |
| 6       | α     | 90°     | 90°     | 90°     | 90°     |
| 7       | β     | 90°     | 90°     | 90°     | 90°     |
| 8       | γ     | 120°    | 120°    | 90°     | 90°     |
| 9       | R$_p$% |         | 11.7    |
| 10      | R$_wp$%|         | 10.6    |
| 11      | χ$^2$  |         | 3.27    |

Table S1. Refinement parameters of MoCot catalyst

| Sr. No. | Parameters | Mo$_2$C | Mo$_2$N |
|---------|------------|---------|---------|
| 1       | Symmetry   | Hexagonal | Cubic  |
| 2       | Space group| 194     | 225     |
|         | Input | Output | Input | Output |
| 3       | a     | 2.99091 Å | 2.99904 Å | 4.16158 Å | 4.18046 Å |
| 4       | b     | 2.99091 Å | 2.99904 Å | 4.16158 Å | 4.18046 Å |
| 5       | c     | 4.71022 Å | 4.76760 Å | 4.16158 Å | 4.18046 Å |
| 6       | α     | 90°     | 90°     | 90°     | 90°     |
| 7       | β     | 90°     | 90°     | 90°     | 90°     |
| 8       | γ     | 120°    | 120°    | 90°     | 90°     |
| 9       | R$_p$% |         | 9.3     |
| 10      | R$_wp$%|         | 11.2    |
| 11      | χ$^2$  |         | 7.33    |

Table S2. Refinement parameters of MoCot1 catalyst
Table S3. Refinement parameters of MoCot2 catalyst

| Sr. No. | Parameters | Mo$_2$C | Mo$_2$N |
|---------|------------|---------|---------|
| 1       | Symmetry   | Hexagonal | Cubic   |
| 2       | Space group | 194 | 225 |
| 3       | a           | 2.99091 Å | 2.98445 Å | 4.16158 Å | 4.16534 Å |
| 4       | b           | 2.99091 Å | 2.98445 Å | 4.16158 Å | 4.16534 Å |
| 5       | c           | 4.71022 Å | 4.77420 Å | 4.16158 Å | 4.16534 Å |
| 6       | α           | 90°      | 90°      | 90°      | 90°      |
| 7       | β           | 90°      | 90°      | 90°      | 90°      |
| 8       | γ           | 120°     | 120°     | 90°      | 90°      |
| 9       | R$_p$%      | 10.2     |          |          |
| 10      | R$_pp$%     | 9.31     |          |          |
| 11      | χ           | 6.43     |          |          |

S3. BET analysis

S3.1. BET analysis of MoCot catalyst

The catalyst was degassed at temperature 200°C for 6hr before BET analysis.

Figure S3. showing Nitrogen adsorption BET isotherms and inset showing BJH pore distribution of the catalyst
S3.2. BET analysis of MoCot1 and MoCot2 catalyst

![BET analysis](image_url)

**Figure S4.** Nitrogen adsorption BET isotherms and inset showing BJH pore distribution of the catalyst (a) MoCot1 and (b) MoCot2

S4. Electrochemical measurements

S4.1. General methodology of electrode fabrication.

The catalyst ink was prepared by dispersing 5 mg of electrocatalyst powder into 500 µL of dimethylformamide containing 5 µL of 5 wt% Nafion and keeping it for 120 min under ultrasonication to form a homogeneous suspension.

Initially, the glassy carbon electrode was polished with alumina powder (0.5-micron size) and used as a working electrode. A well-dispersed ink of 5 µL was coated onto the surface of a working electrode (GCE, 3 mm in diameters) by means of the drop-casting method and dried under vacuum. The electrochemical measurements were recorded in argon saturated 0.5 M H₂SO₄ solution at a scan rate of 5 mVs⁻¹. The commercially available Pt/C (20wt %) catalyst was also tested under similar conditions. Electrochemical stability tests were conducted up to 3000 LSV cycles in the same potential range as above but at a faster scan rate of 8 mV sec⁻¹.
S4.2. Linear sweep voltammetry (LSV) measurements of all the catalysts

A comparative study of the LSV measurements was done as follows:

a) MoCot: Shows overpotential of 167 mV

b) MoCot-m: A physical mixture of Mo$_2$C and Mo$_2$N was also prepared with keeping the same composition as obtained in the MoCot catalyst to study and compare its electrochemical behaviour. The overpotential of the mixture (MoCot-m) was found to be 252 mV in driving a current density of 10 mA/cm$^2$.

c) MoCot1: Shows overpotential of 263 mV.

d) MoCot2: Shows overpotential of 287 mV.

Figure S5. Electrocatalytic measurements of electrodes for hydrogen evolution in 0.5 M H$_2$SO$_4$ solution.
S4.3. Linear sweep voltammetry (LSV) measurements of MoCot in alkaline and neutral media.

![Linear sweep voltammetry (LSV) measurements](image)

Figure S6. Polarisation Curve of MoCot catalyst in (a) 0.5M KOH and (b) 1.5M potassium phosphate solution (pH~7)

S5. PXRD measurement

S5.1. PXRD measurements of as-synthesized Mo$_2$C and Mo$_2$N

![PXRD patterns of as-synthesized Mo$_2$C and Mo$_2$N](image)

Figure S7. PXRD patterns of as-synthesized (a) Mo$_2$C and (b) Mo$_2$N
S5.2. PXRD measurement of the catalyst after stability test

Powder X-ray Diffraction pattern of MoCot catalyst recovered after 2500 LSV cycles showing the retention of catalyst composition and structure.

![PXRD pattern of MoCot catalyst](image)

**Figure S8.** PXRD patterns of isolated electrocatalyst after a durability test of 2500 cycle.

S6. XPS fitting parameters

| Element | Peak                | BE (eV)               | FWHM         | Area (%)   |
|---------|---------------------|-----------------------|--------------|------------|
| Mo3d    | Mo$^{2+}$ (Mo$_2$C) | 228.4 and 231.5       | 1.032 and 1.032 | 21.66 and 28.92 |
|         | Mo$^{4+}$ (MoO$_2$) | 229.2 and 232.4       | 1.048 and 1.048 | 8.87 and 22.94    |
|         | Mo$^{5+}$ (Mo$_4$O$_{11}$) | 235.1   | 1.050       | 9.04     |
|         | Mo$^{6+}$ (MoO$_3$) | 235.9               | 1.061       | 9.74     |
| C1s     | C-Mo (Mo$_2$C)      | 283.8                 | 1.070       | 59.91     |
|         | C=C (Carbon)        | 284.7                 | 1.079       | 40.08     |
| Mo3p-N1s| Mo$^{2+}$ (Mo$_2$N) | 395.3                 | 3.792       | 37.22     |
|         | Mo$^{4+}$ (MoO$_3$) | 398.8                 | 3.812       | 62.77     |

**Table S4.** Deconvoluted XPS peak positions of Mo3d, C1s and Mo3p-N1s with corresponding binding energy and FWHM