Supplementary Information

Multimetallic assembly of concave-shaped rectangular Mn_4 clusters as efficient hydrogen evolution electrocatalysts

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Figures with Captions

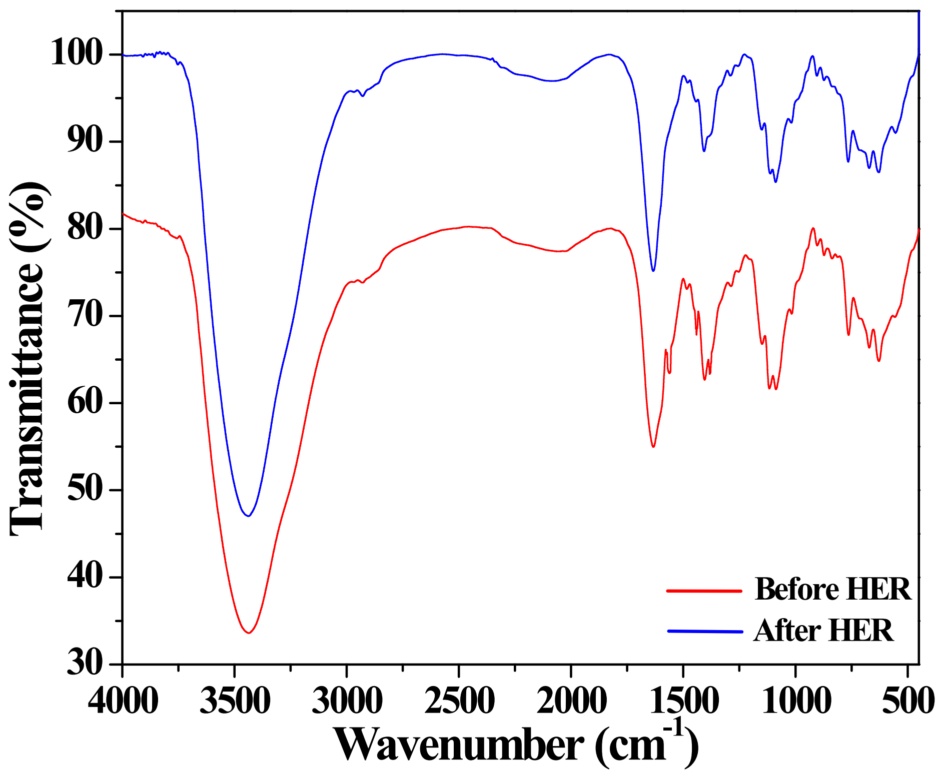


Fig. S1. FTIR spectra of **1** before (—) and after (—) HER studies in the region of 4000-450 cm^{-1}.

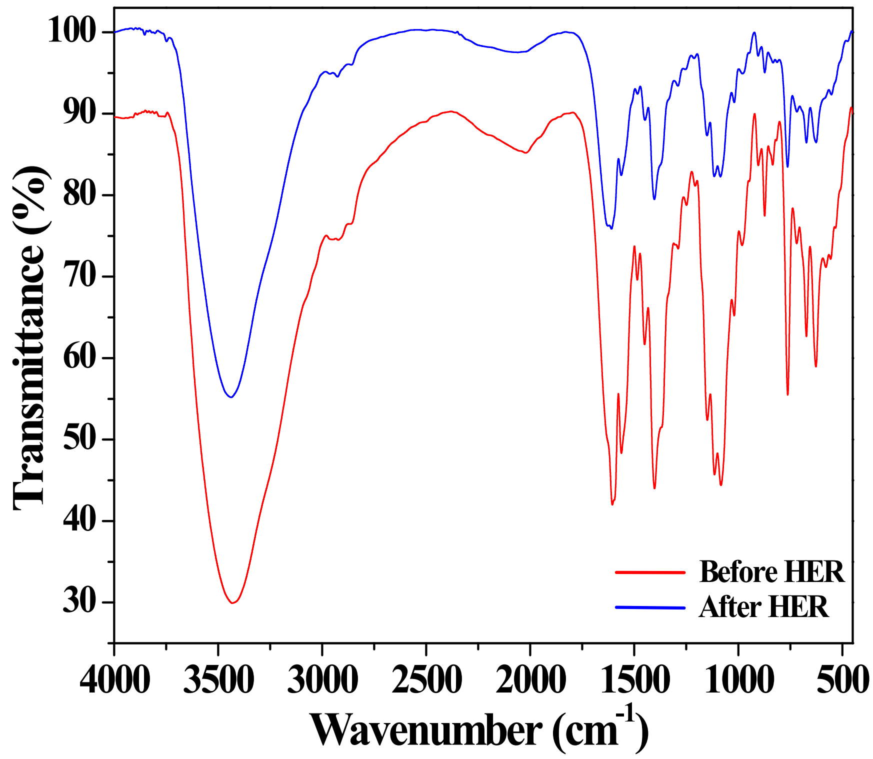


Fig. S2. FTIR spectra of **2** before (—) and after (—) HER studies in the region of 4000-450 cm^{-1}.

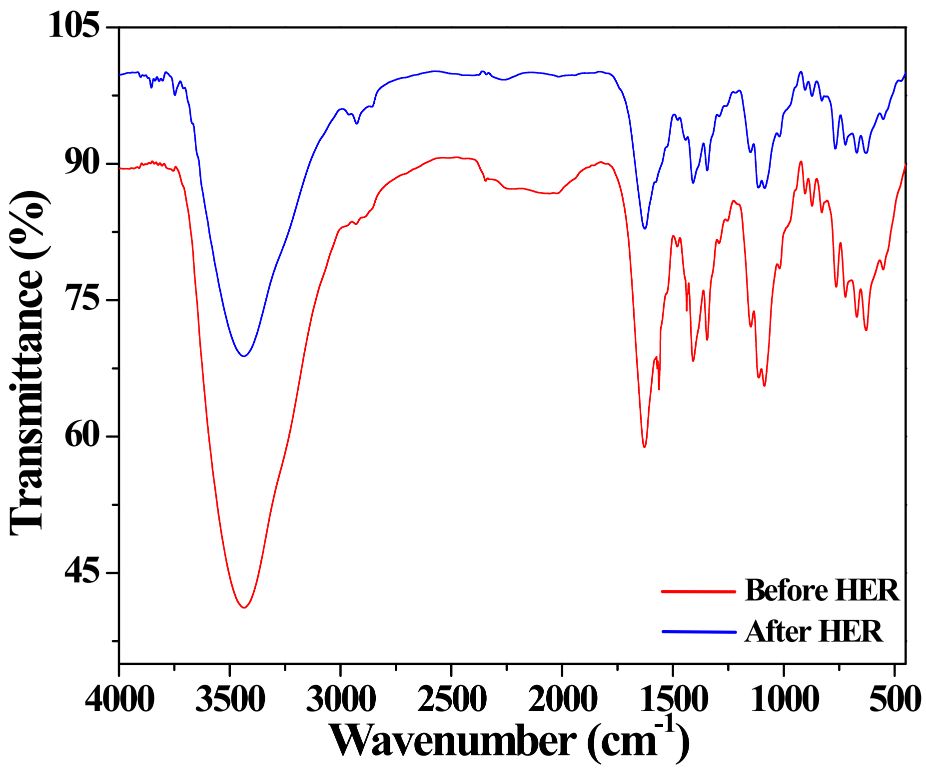


Fig. S3. FTIR spectra of **3** before (—) and after (—) HER studies in the region of 4000-450 cm^{-1}.

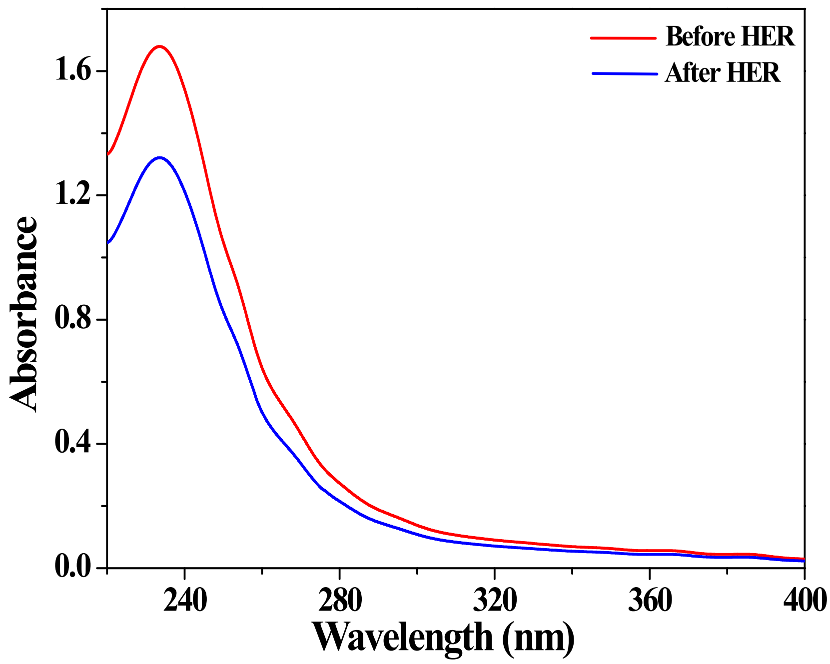


Fig. S4. UV-Vis spectra of **1** at 10^{-4} (M) in MeOH before (—) and after (—) HER studies.

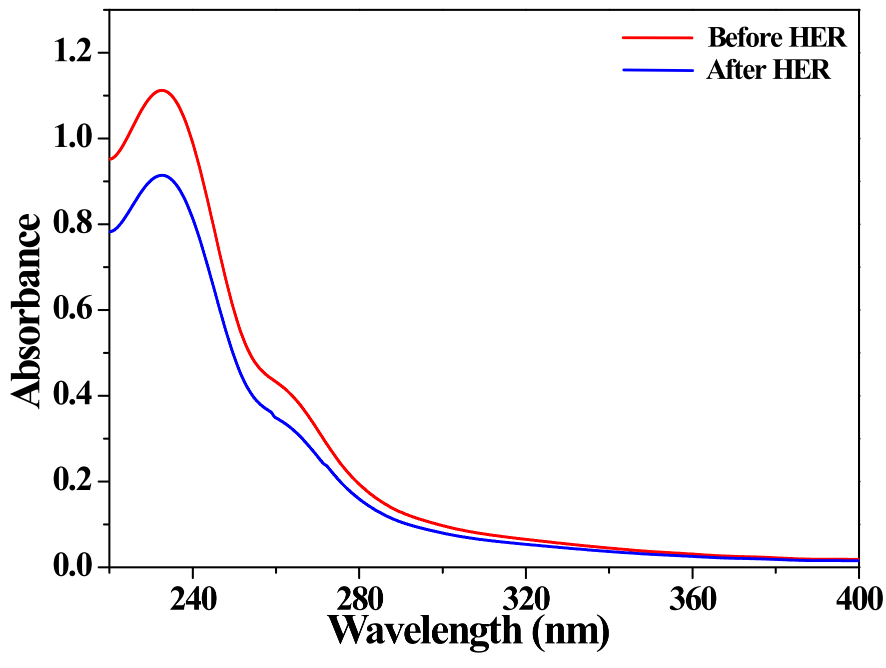


Fig. S5. UV-Vis spectra of **2** at 10^{-4} (M) in MeOH before (—) and after (—) HER studies.

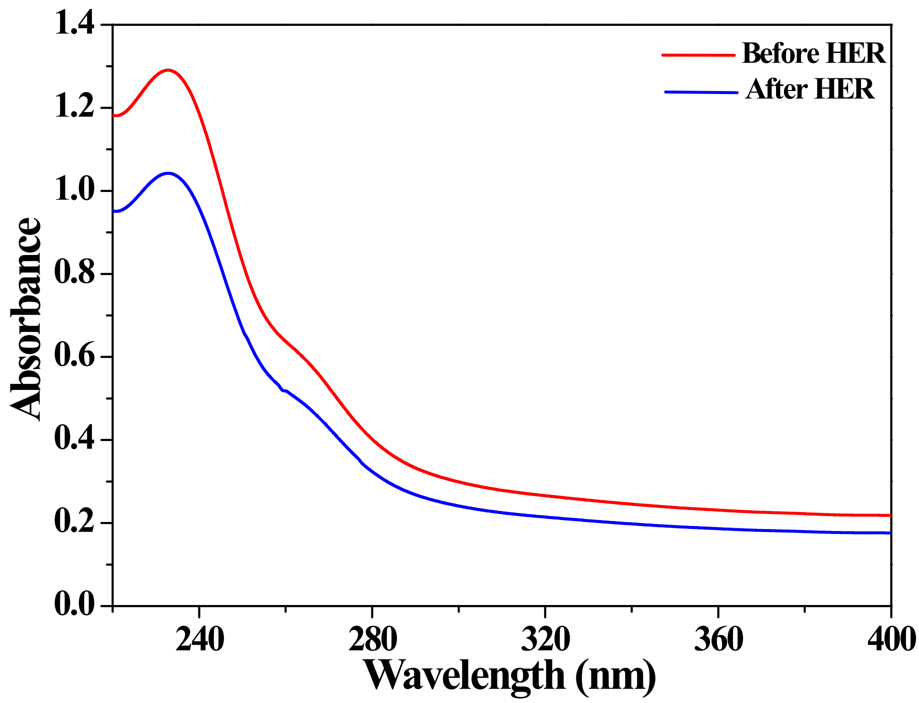


Fig. S6. UV-Vis spectra of **3** at 10^{-4} (M) in MeOH before (—) and after (—) HER studies.

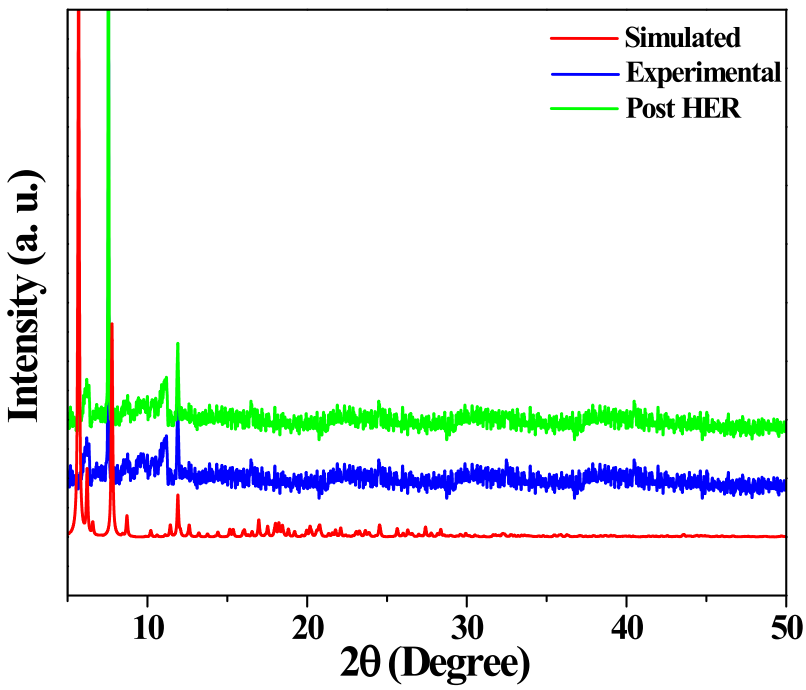


Fig. S7. Powder X-ray diffraction (PXRD) patterns of **1**: simulated PXRD (—), pre-HER experimental PXRD (—), and post-HER experimental PXRD (—).

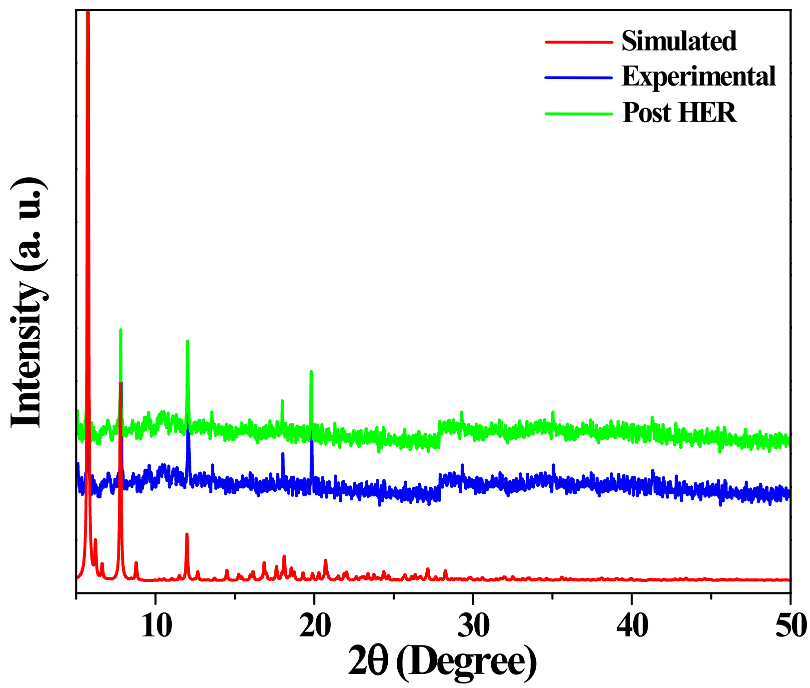


Fig. S8. Powder X-ray diffraction (PXRD) patterns of **2**: simulated PXRD (—), pre-HER experimental PXRD (—), and post-HER experimental PXRD (—).

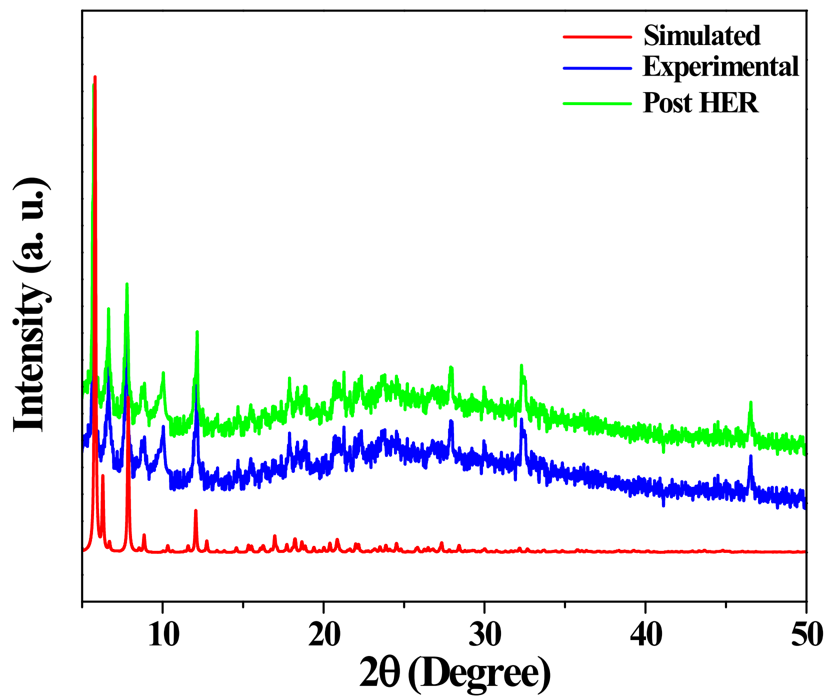


Fig. S9. Powder X-ray diffraction (PXRD) patterns of **3**: simulated PXRD (—), pre-HER experimental PXRD (—), and post-HER experimental PXRD (—).

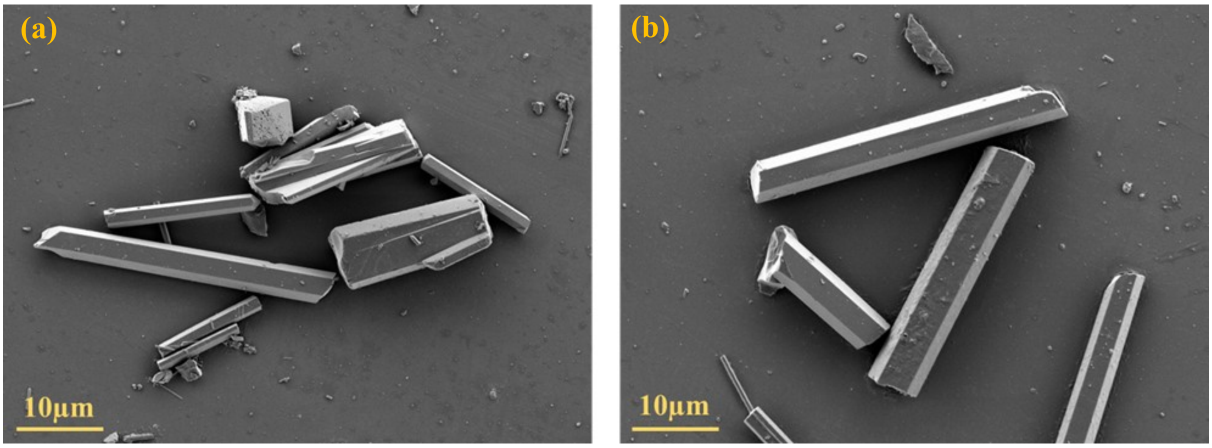


Fig. S10. Field emission scanning electron microscopic (FESEM) image of **1** (a) before and (b) after the HER studies.

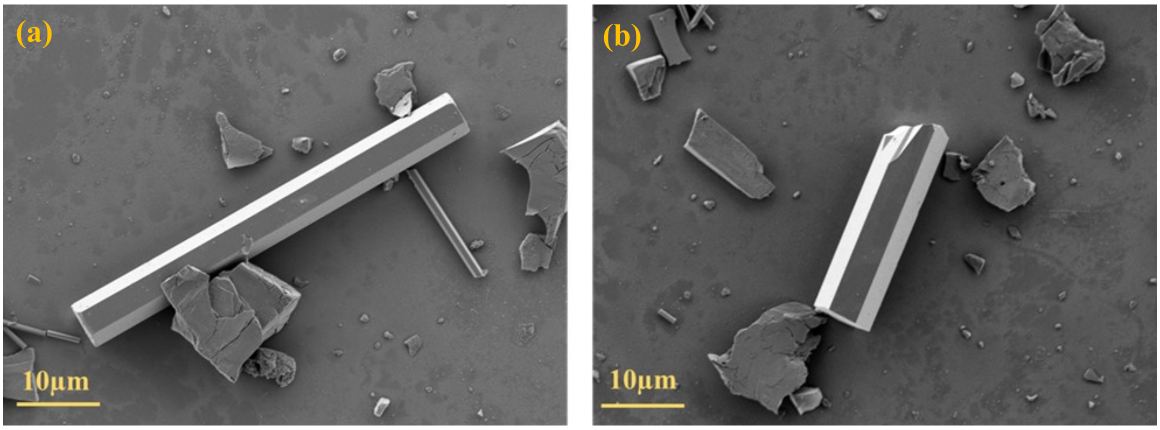


Fig. S11. Field emission scanning electron microscopic (FESEM) image of **2** (a) before and (b) after the HER studies.

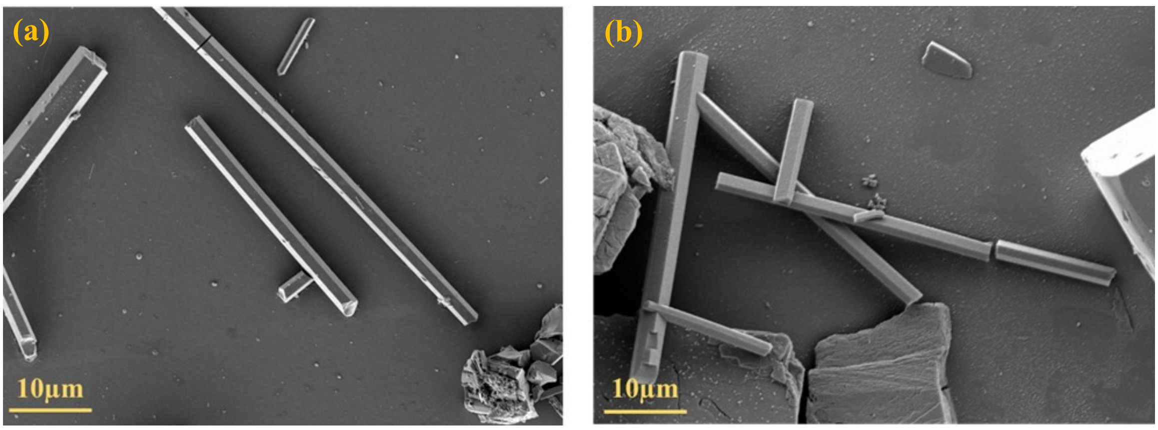
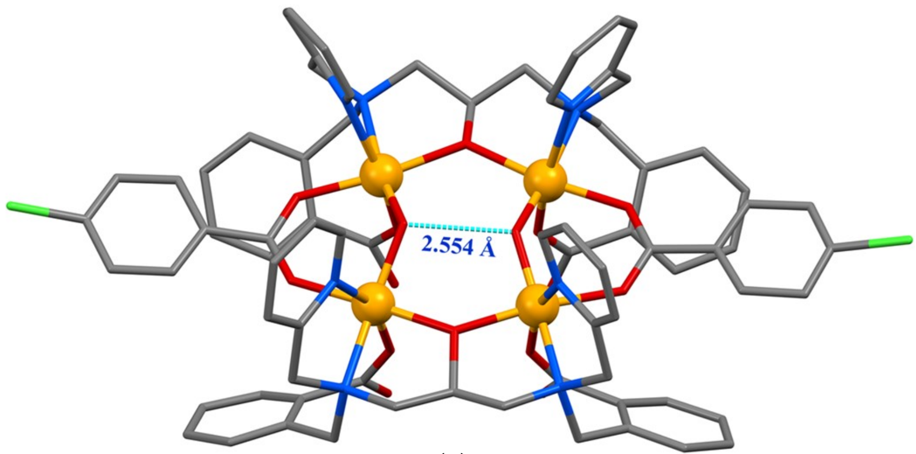
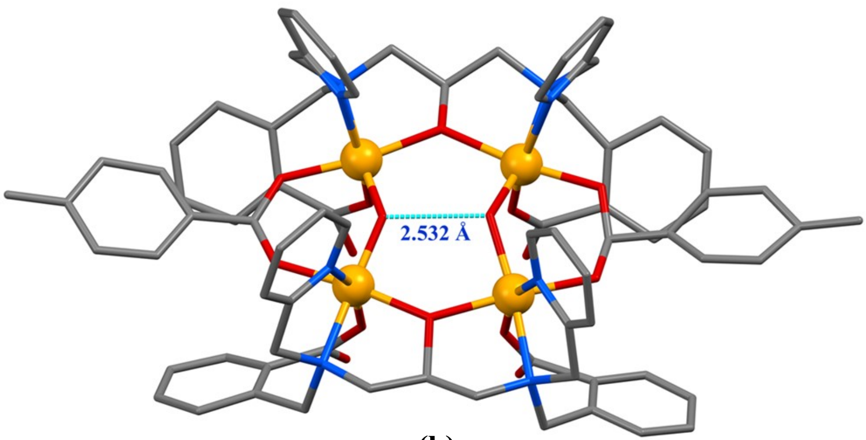


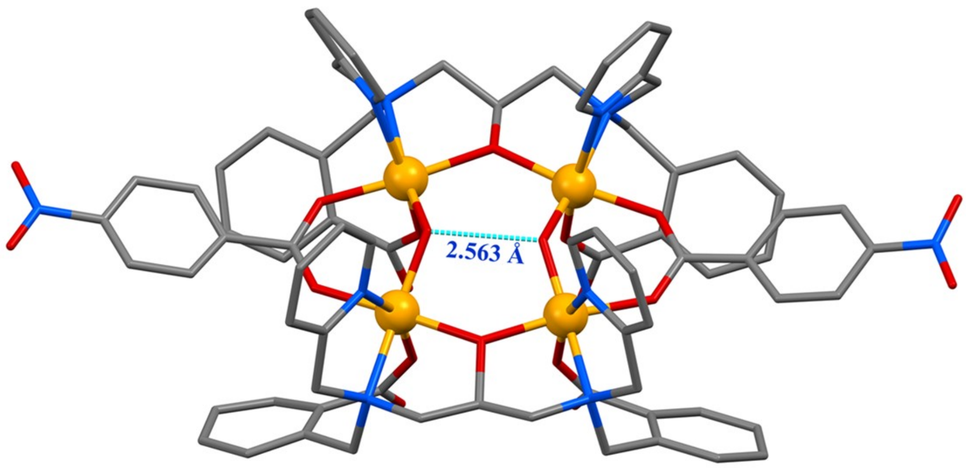
Fig. S12. Field emission scanning electron microscopic (FESEM) image of **3** (a) before and (b) after the HER studies.



(a)



(b)



(c)

Fig. S13. Views of **1** (a), **2** (b) and **3** (c) showing intra-molecular H-bonds with interatomic distances of 2.554, 2.563 and 2.532 Å respectively, between the O2 and O3 atoms.

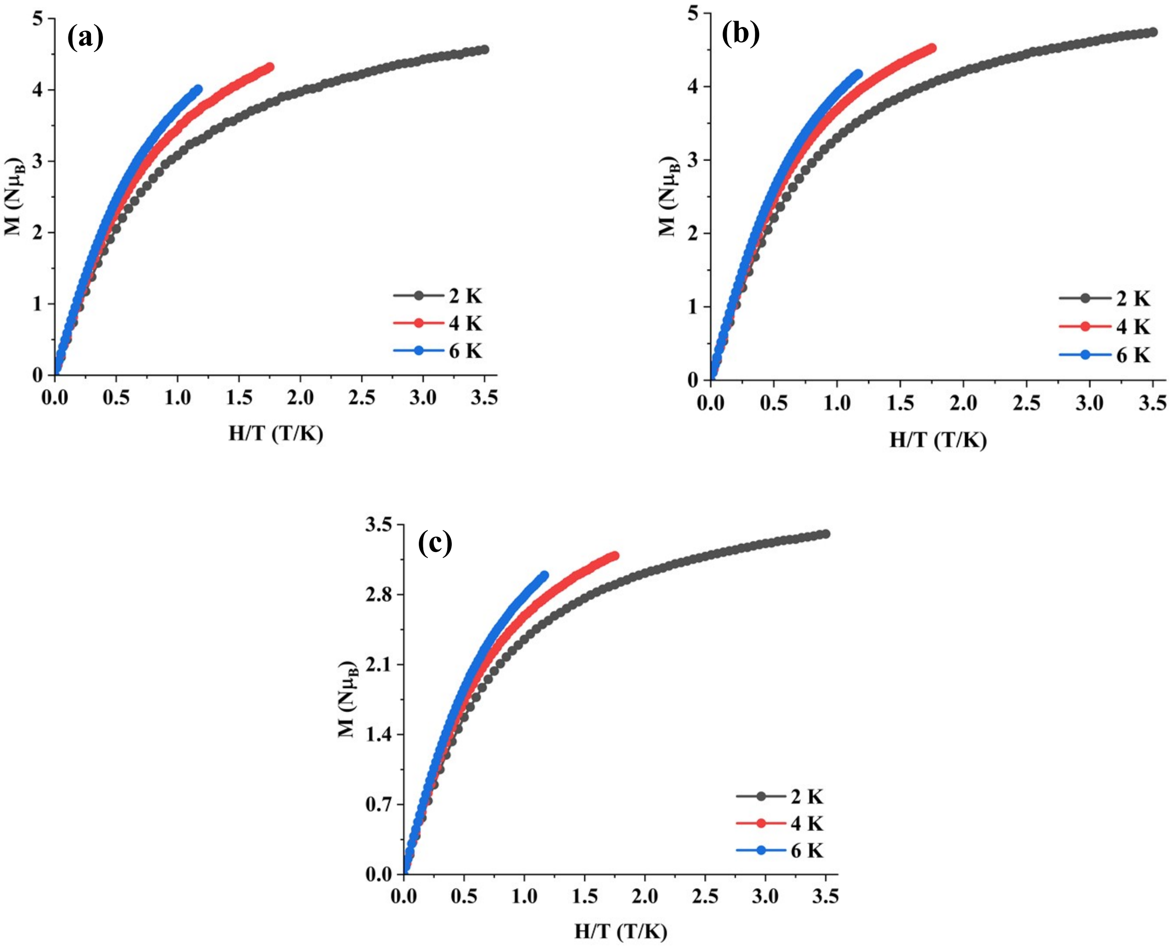


Fig. S14. Reduced magnetization data (M *vs.* H/T) for (a) **1**, (b) **2** and (c) **3** collected under varying applied dc field.

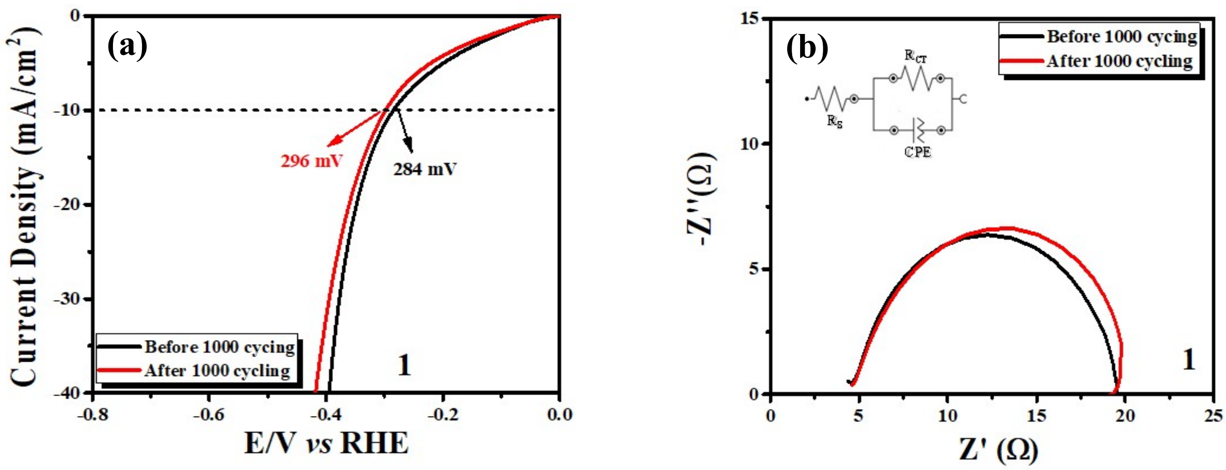


Fig. S15. (a) LSV outcomes and (b) EIS results of **1** before and after HER AD studies, respectively.

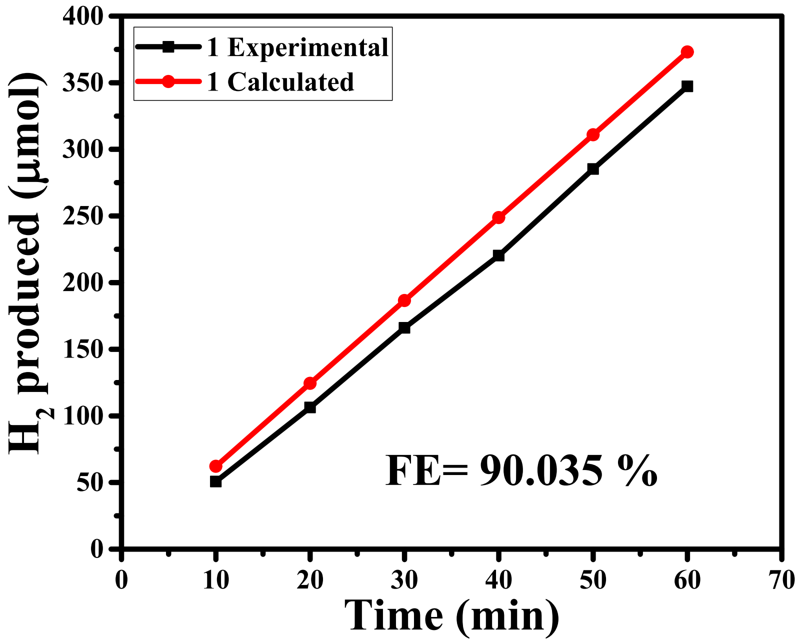
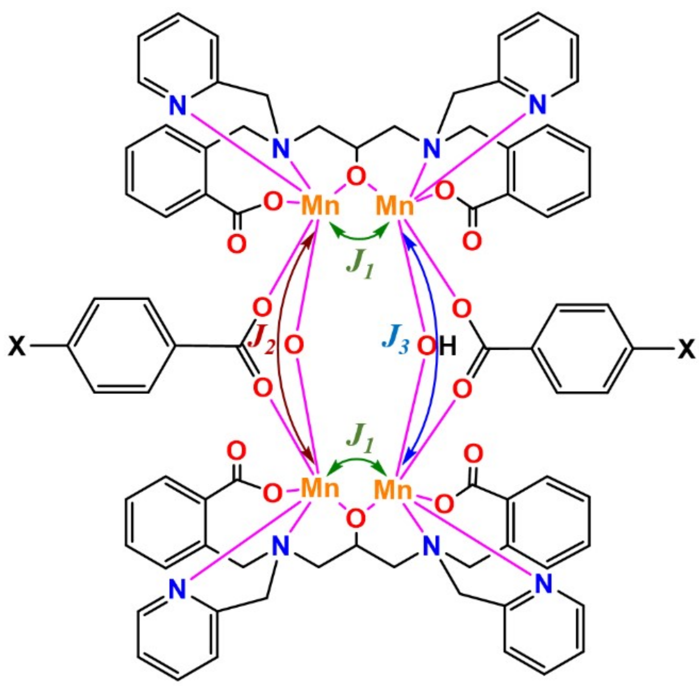


Fig. S16. Representative plot for Faradic efficiency of catalyst **1**.

Scheme with Caption



Scheme S1. A schematic diagram showing the pathways for magnetic exchange interactions in **1-3**.

Tables with Captions

Table S1. Selected bond distances (Å) and angles (deg) in **2.**

Bond distances (Å)			
Mn(1)-O(1)	2.020(12)	Mn(2)-O(1)	2.076(12)
Mn(1)-O(2)	1.812(7)	Mn(2)-O(3)	1.951(10)
Mn(1)-O(4)	2.136(15)	Mn(2)-O(6)	2.155(16)
Mn(1)-O(8)	1.945(13)	Mn(2)-O(9)	1.976(15)
Mn(1)-N(1)	2.120(16)	Mn(2)-N(3)	2.215(16)
Mn(1)-N(2)	2.206(18)	Mn(2)-N(4)	2.270(2)
Bond angles (deg)			
O(1)-Mn(1)-O(2)	93.6(6)	O(1)-Mn(2)-O(3)	90.2(6)
O(1)-Mn(1)-O(4)	89.9(5)	O(1)-Mn(2)-O(6)	88.4(5)
O(1)-Mn(1)-O(8)	172.2(6)	O(1)-Mn(2)-O(9)	172.2(6)
O(1)-Mn(1)-N(1)	83.0(6)	O(1)-Mn(2)-N(3)	82.0(5)
O(1)-Mn(1)-N(2)	91.7(6)	O(1)-Mn(2)-N(4)	95.4(6)
O(2)-Mn(1)-O(4)	98.6(7)	O(3)-Mn(2)-O(6)	104.4(6)
O(2)-Mn(1)-O(8)	93.7(7)	O(3)-Mn(2)-O(9)	94.7(7)
O(2)-Mn(1)-N(1)	171.7(7)	O(3)-Mn(2)-N(3)	165.1(7)
O(2)-Mn(1)-N(2)	98.9(8)	O(3)-Mn(2)-N(4)	92.8(7)
O(4)-Mn(1)-O(8)	91.9(6)	O(6)-Mn(2)-O(9)	96.2(7)
O(4)-Mn(1)-N(1)	89.0(6)	O(6)-Mn(2)-N(3)	88.1(6)
O(4)-Mn(1)-N(2)	162.3(6)	O(6)-Mn(2)-N(4)	162.4(7)
O(8)-Mn(1)-N(1)	89.4(6)	O(9)-Mn(2)-N(3)	91.8(6)
O(8)-Mn(1)-N(2)	84.3(6)	O(9)-Mn(2)-N(4)	78.4(7)
N(1)-Mn(1)-N(2)	73.7(7)	N(3)-Mn(2)-N(4)	75.5(7)

Table S2. Selected bond distances (Å) and angles (deg) in **3.**

Bond distances (Å)			
Mn(1)-O(1)	2.004(5)	Mn(2)-O(1)	2.062(4)
Mn(1)-O(2)	1.818(3)	Mn(2)-O(3)	1.937(3)
Mn(1)-O(4)	2.133(5)	Mn(2)-O(6)	2.154(6)
Mn(1)-O(8)	2.000(5)	Mn(2)-O(10)	1.973(7)
Mn(1)-N(1)	2.134(6)	Mn(2)-N(3)	2.210(6)
Mn(1)-N(2)	2.255(6)	Mn(2)-N(4)	2.290(8)
Bond angles (deg)			
O(1)-Mn(1)-O(2)	93.8(2)	O(1)-Mn(2)-O(3)	91.4(2)
O(1)-Mn(1)-O(4)	98.7(2)	O(1)-Mn(2)-O(6)	88.55(18)
O(1)-Mn(1)-O(8)	172.6(2)	O(1)-Mn(2)-O(10)	176.2(4)
O(1)-Mn(1)-N(1)	83.5(2)	O(1)-Mn(2)-N(3)	83.2(2)
O(1)-Mn(1)-N(2)	92.6(2)	O(1)-Mn(2)-N(4)	94.9(3)
O(2)-Mn(1)-O(4)	98.7(2)	O(3)-Mn(2)-O(6)	103.8(2)
O(2)-Mn(1)-O(8)	93.4(2)	O(3)-Mn(2)-O(10)	91.3(3)
O(2)-Mn(1)-N(1)	171.6(3)	O(3)-Mn(2)-N(3)	165.8(2)
O(2)-Mn(1)-N(2)	98.2(3)	O(3)-Mn(2)-N(4)	94.9(2)
O(4)-Mn(1)-O(8)	91.7(2)	O(6)-Mn(2)-O(10)	93.4(4)
O(4)-Mn(1)-N(1)	89.3(2)	O(6)-Mn(2)-N(3)	89.24(19)
O(4)-Mn(1)-N(2)	163.0(2)	O(6)-Mn(2)-N(4)	161.0(2)
O(8)-Mn(1)-N(1)	89.1(2)	O(10)-Mn(2)-N(3)	93.6(3)
O(8)-Mn(1)-N(2)	85.0(2)	O(10)-Mn(2)-N(4)	82.2(5)
N(1)-Mn(1)-N(2)	74.0(2)	N(3)-Mn(2)-N(4)	72.7(2)

Table S3. Values of magnetic coupling constant, Landé g-factor and zero-field splitting parameters of **1-3**.

Complex	$g_x = g_y$	g_z	$2J_1$	$2J_2$	$2J_3$	D
1	2.17	2.56	-11.38	-13.41	+5.92	-0.47
2	2.33	1.91	-7.98	-11.92	+4.44	-0.42

3	2.11	2.43	-10.04	-9.40	+7.64	-1.43

Calculation for the Cost of the Synthesized Electrocatalysts (1-3) and the Price of the Generated Hydrogen

To gain idea about the cost of the synthesized electrocatalysts (**1-3**), we need to know the materials used for their synthesis. Thus, a list of materials used and their cost are given below:

Sl. No.	Description	Specification	Amount (Rs.)
1.	1,3-Diamino-2-propanol	25 g	7140.00
2.	2-Carboxybenzaldehyde	100 g	12004.93
3.	2-Picolylchloride hydrochloride	25 g	9,768.00
4.	Sodium borohydride	100 g	2460.00
5.	Manganese carbonate	500 g	338.00
6.	Sodium hydroxide	500 g	566.00
7.	*Para*-chlorobenzoic acid	25 g	2700.00
8.	*Para*-methylbenzoic acid	25 g	1800.00
9.	*Para*-nitrobenzoic acid	25 g	1700.00
10.	Perchloric acid	500 mL	1044.00
11.	Hydrochloric acid	2.5 L	1310.00
12.	Hydrobromic acid	500 mL	800.00
13.	Lithium hydroxide	100 g	3278.00
14.	Methanol	2.5 L	555.00
15.	Diethyl ether	2.5 L	3021.00

Synthesis of the Multifunctional Organic Scaffold (H_3L):

4.643 g 2-carboxybenzaldehyde + 1.1424 g 1,3-diamino-2-propanol = 4.95 g precursor organic scaffold (87%).

1.790 g precursor organic scaffold + 1.640 g 2-picolylchloride hydrochloride = 2.00 g final organic scaffold.

NaOH used: 1.20 g, LiOH used: 1.10 g, $NaBH_4$ used: 1.50 g, methanol used: ~ 30 mL, HCl used: ~ 5 mL, HBr used: ~ 2 mL.

Synthesis of Mn_4 Catalysts:

Multifunctional organic scaffold used: 250 mg, metal salts used: 333 mg, NaOH used: 42 mg, methanol used: ~ 20 mL, diethyl ether used: ~ 50 mL.

Catalyst **1:** Yield: 0.341 g (75%): *para*-chlorobenzoic acid used: 72 mg.

Catalyst **2:** Yield: 0.321 g (73%): *para*-methylbenzoic acid used: 63 mg.

Catalyst **3:** Yield: 0.321 g (73%): *para*-nitrobenzoic acid used: 78 mg.

Now, the calculation for the cost of the synthesized catalysts is given below:

Synthesis of the Multifunctional Organic Scaffold (H_3L):

- **2-Carboxybenzaldehyde used**: 4.643 g
  Cost = (4.643/100)×12004.93 = Rs.557.19
- **1,3-Diamino-2-propanol used**: 1.1424 g
  Cost = (1.1424/25)×7140.00 = Rs.326.31
- **2-Picolylchloride hydrochloride used**: 1.640 g
  Cost = (1.640/25)×9768.00 = Rs.640.99
- **Sodium hydroxide (NaOH) used**: 1.20 g
  Cost = (1.20/500)×566.00 = Rs.1.36
- **Lithium hydroxide (LiOH) used**: 1.10 g
  Cost = (1.10/100)×3278.00 = Rs.36.06
- **Sodium borohydride ($NaBH_4$) used**: 1.50 g
  Cost = (1.50/100)×2460.00 = Rs.36.90
- **Methanol used**: 30 mL
  Cost = (30/2500)×555.00 = Rs.6.66
- **Hydrochloric acid (HCl) used**: 5 mL
  Cost = (5/2500)×1310.00 = Rs.2.62
- **Hydrobromic acid (HBr) used**: 2 mL
  Cost = (2/500)×800.00 = Rs.3.20
- **Total Cost of H_3L= Rs.1611.29**

Synthesis of the Electrocatalysts (**1-3**):

For each electrocatalyst,

- **H_3L used**: 250 mg

  Cost = (250/2000)×Rs.1611.29 = Rs. 201.41

- **Metal salt used**: 333 mg

  Cost = Rs. 50.00 (approx.)

- **NaOH used**: 42 mg
  Cost = (42/500)×566.00 = Rs.0.048

- **Methanol used**: 20 mL
  Cost = (20/2500)×555.00 = Rs.4.44

- **Diethyl ether used**: 50 mL
  Cost = (50/2500)×3021.00 = Rs.60.42

- **Benzoic acid derivatives:**

  - ***Para*-chlorobenzoic acid used for catalyst 1**: 72 mg
    Cost = (72/25000)×2700.00 = Rs.7.78

  - ***Para*-methylbenzoic acid used for catalyst 2**: 63 mg
    Cost = (63/25000)×1800.00 = Rs.4.54

  - ***Para*-nitrobenzoic acid used for catalyst 3**: 78 mg
    Cost = (78/25000)×1700.00 = Rs.5.30

For **catalyst 1**, the total cost: Rs. 324.10
For **catalyst 2**, the total cost: Rs. 320.86
For **catalyst 3**, the total cost: Rs. 321.62

Cost of the Synthesized Electrocatalysts:

The average cost per gram of synthesized electrocatalyst: Rs.987.42

The average cost per 50 mg of the synthesized electrocatalyst = (50/1000)×987.42 = Rs.49.37

Additionally, the **carbon cloth** costs at Rs.10,000 per square meter contributes as follows for 4.5 × 1 cm^2 = (0.045 m^2) × Rs. 10,000 = Rs. 45.00

Here, only the cost of materials used has been discussed, and accordingly, all the calculations are being carried out. But actually, the instruments used for all the characterizations, synthetic processes, experimental works, electrodes, electricity, and operational cost should be considered for a full economic evaluation.

Price of the Generated Hydrogen:

To get an idea of the price of generated hydrogen Faradic efficiency was measured for the best active catalyst **1** using GC, and we have compared the calculated amount of H_2 (from the

Faraday's law) and experimentally obtained H_2 at 20 mA/cm^2 current density (Fig. S16, Supplementary Information). The calculated Faradic efficiency value at the same current density is 90.035 % for catalyst **1**.

Now, Using Faradaic efficiency = 90.035% at 20 mA/cm^2 current density:

- **Charge Passed (Q)**:
  $Q = It = (20\times10^{-3}A)\times(3600s) = 72\ C$
- **Moles of Hydrogen (H_2) Produced**:
  $n = Q$*Faradaic efficiency/$2F = 72*0.90035/2\times96485 = 3.36\times10^{-4}$ moles
- **Mass of H_2 Produced**: $m = n\times M = (3.36\times10^{-4})\times2.016 = 6.78\times10^{-4}$ g
- **Volume of H_2 Produced**: $V = n\times22.414 = (3.36\times10^{-4})\times22.414 = 7.53$ mL

Cost Estimation for Hydrogen Production:

- **Catalyst cost used (1 mg in electrode)**

Cost = Rs. 49.37/50×1 = Rs. 0.987

- **Carbon cloth cost for 1 × 1 cm^2**

Cost = Rs. 10000/10000×1 = Rs. 1.00

Total Cost for Hydrogen Production (1 cm^2 coated electrode)

Total cost = Rs. 0.987 + Rs. 1.00 = Rs. 1.987

Hydrogen cost per Gram

Rs. $1.987/6.78\times10^{-4}$ = Rs.2930.68

Conclusion:

- **Cost per gram of synthesized electrocatalyst**: Rs. 987.42
- **Cost per 50 mg of catalyst**: Rs. 49.37
- **Carbon cloth cost for electrode**: Rs. 45.00
- **Hydrogen production efficiency**: 90.035%
- **Estimated volume of H_2 produced at STP (for 1-hour electrolysis at 1 cm^2)**: 7.53 mL
- **Total cost of hydrogen production**: Rs. 1.987
- **Price per gram of generated hydrogen**: Rs. 2930.68

Although the above calculations deliver a general idea of lab-scale hydrogen production costs, it is vital to emphasize that material optimizations and large-scale synthesis could significantly improve economic viability. Our prime objective is not just cost estimation but to contribute to a sustainable future by producing green hydrogen. With its high energy density and zero carbon dioxide emission, hydrogen emerges as a promising alternative to fossil fuels. Thus, advancing electrocatalyst effectiveness and exploring cost-effective fabrication strategies will further strengthen hydrogen's role as a clean and sustainable energy source.