Supporting Information

Thermochemical synthesis of Mo nano/microspheres: Growth kinetics, electrocatalytic hydrogen evolution, and DFT insights

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1. SEM microstructures

The micrographs of the reaction product obtained from the MoO_3+10Zn mixture after the temperature surge. They illustrate the morphology of the product before and after acid purification.

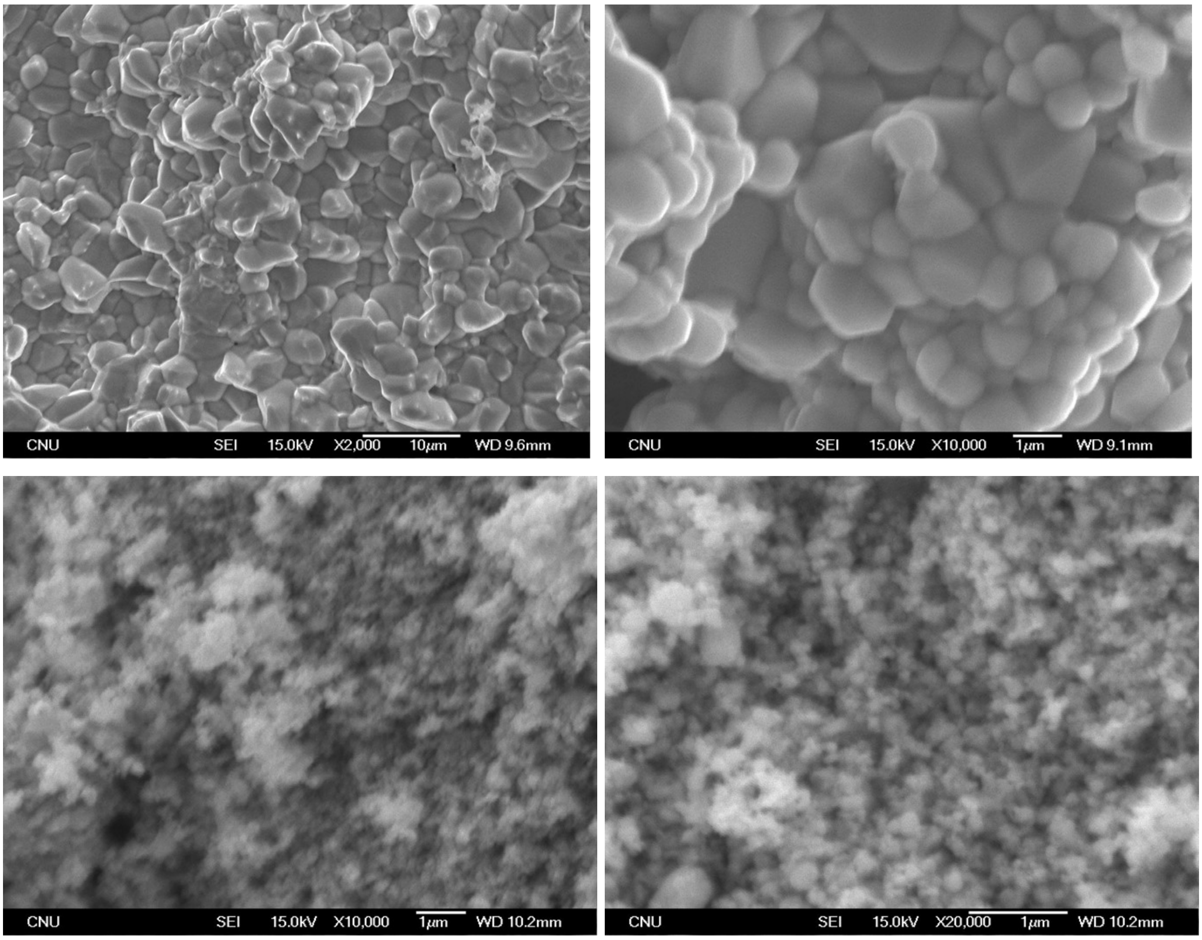


Fig. S1. SEM micrographs of various magnifications: (a, b) reaction product (c, d) purified product (Mo+10Zn).

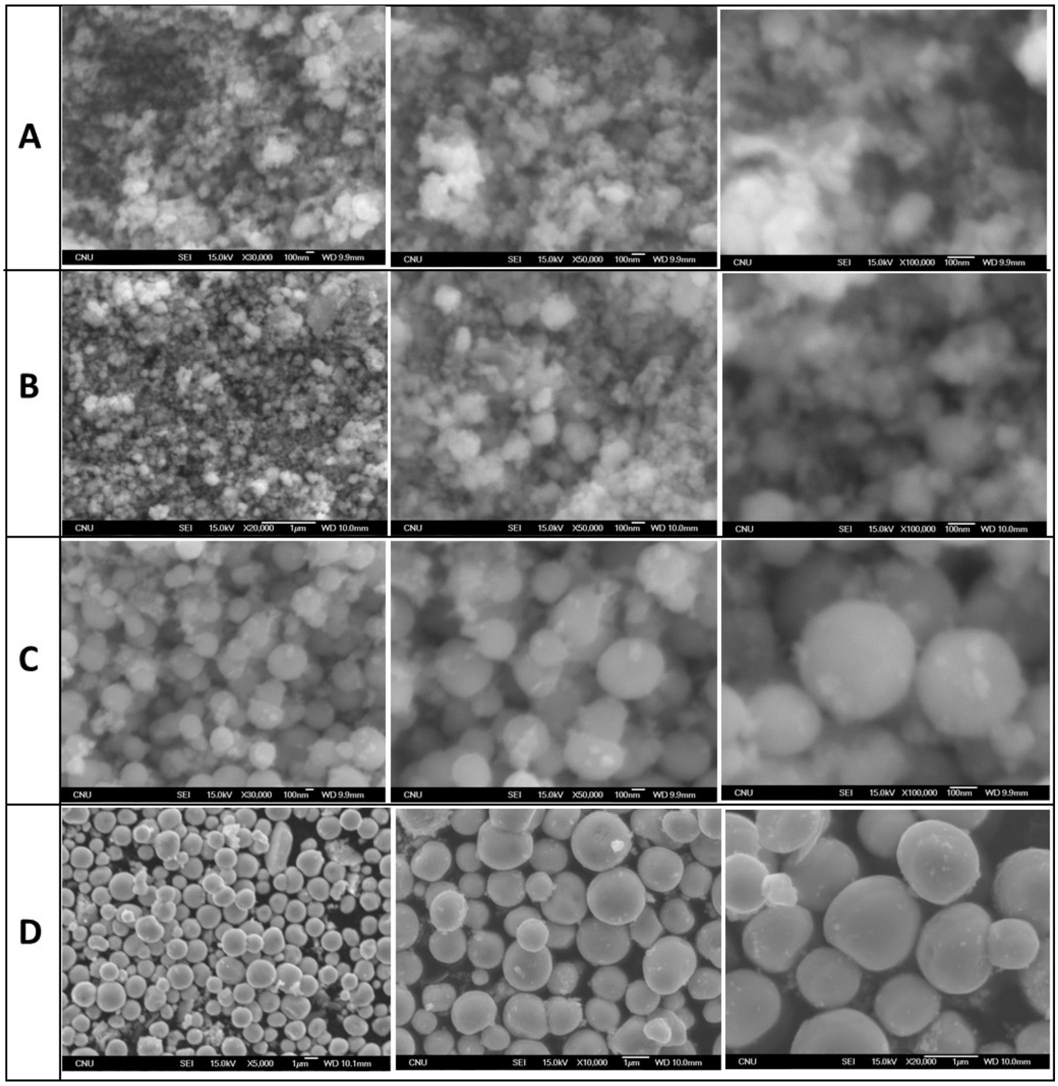


Fig. S2. SEM images of Mo samples prepared from MoO_3+10Zn mixture at different processing temperatures for 2 hours: **A.** 500 ^{o}C; **B.** 600 ^{o}C; **C.** 700 ^{o}C and **D.** 800 ^{o}C.

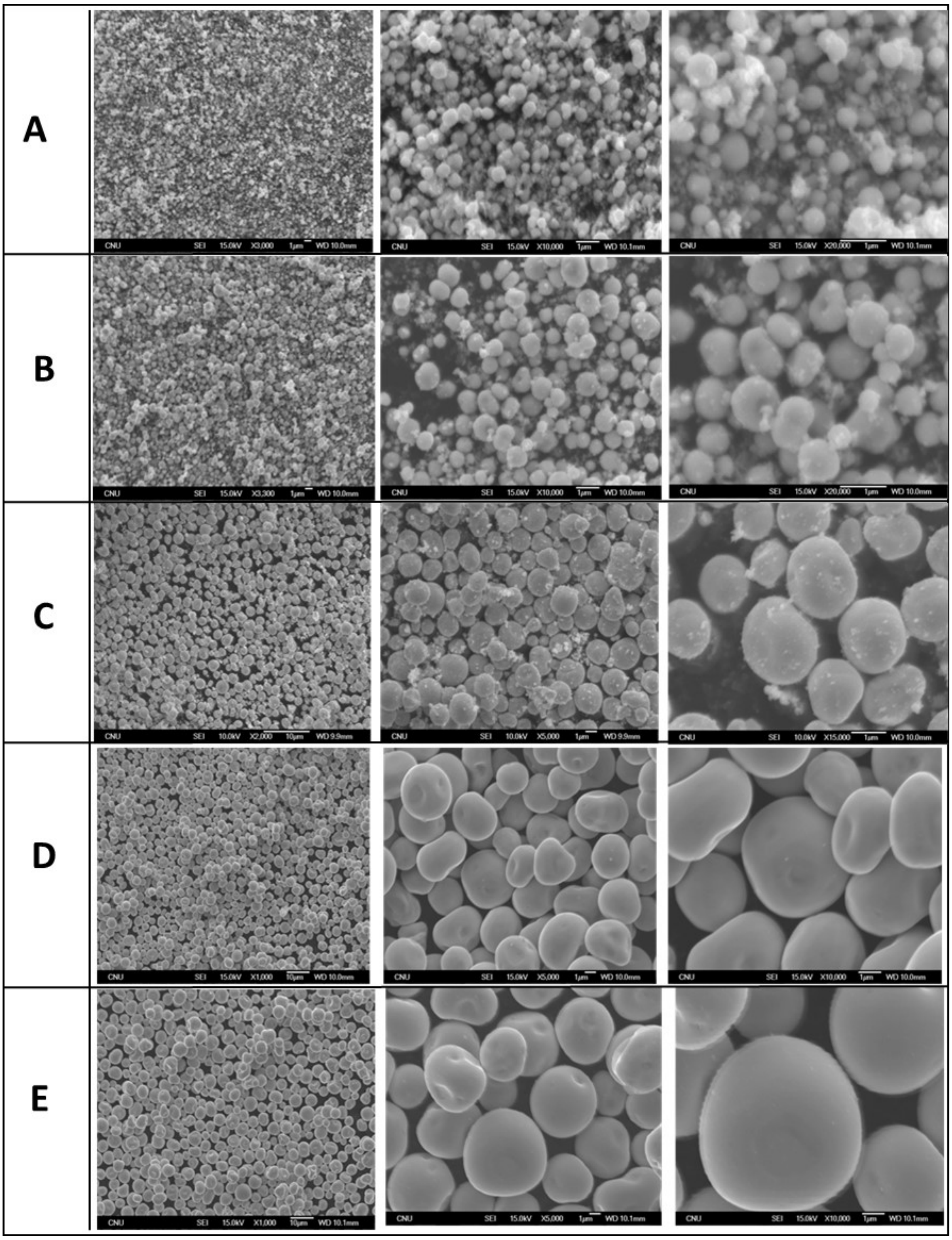


Fig. S3. SEM images of Mo samples prepared from MoO_3+10Zn mixture at 800 ^{o}C for different processing times (hours): **A.** 0.17; **B.** 0.5; **C.** 2; **D.** 10.0; **E**. 20.0.

2. SEM/EDS mapping

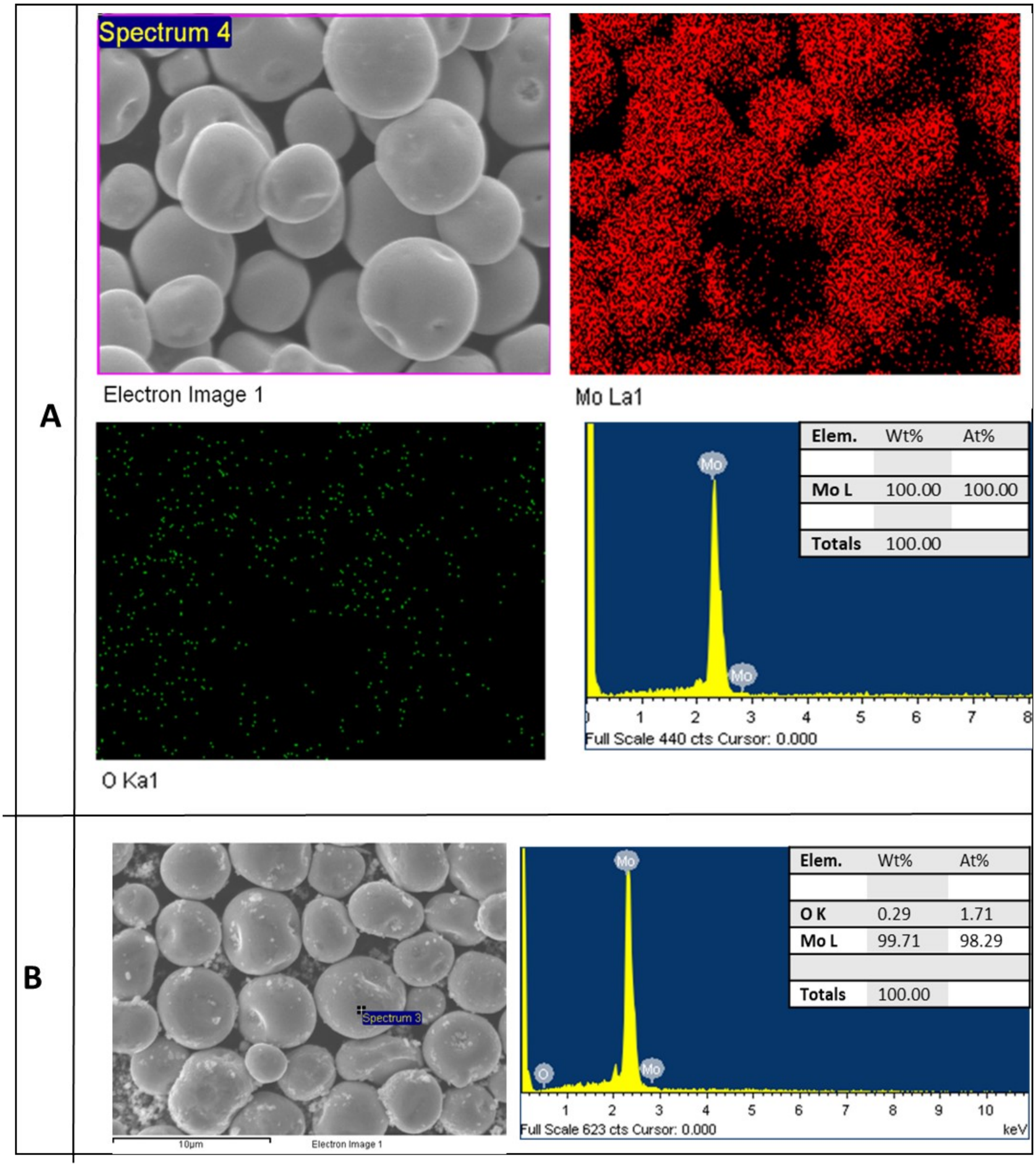


Fig. S4. **A.** SEM/EDS mapping of Mo microspheres derived at 800 °C for 20 hours; **B.** SEM/EDS spectra of Mo microsphere derived at 800 °C for 10 hours.

3. XPS spectras

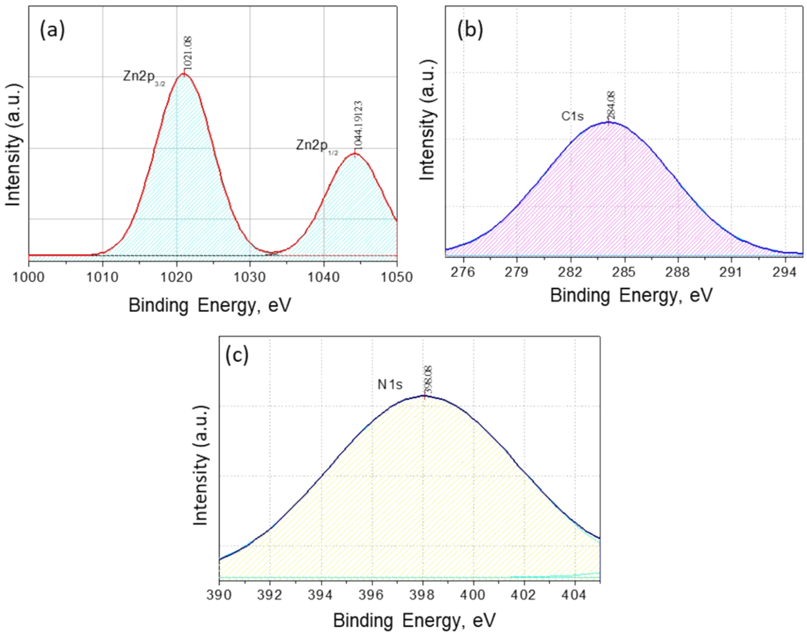


Fig. S5. Gaussian fitting of Zn2p, C1s and N1s elements in Mo powder.

4. WO_3+7Zn system

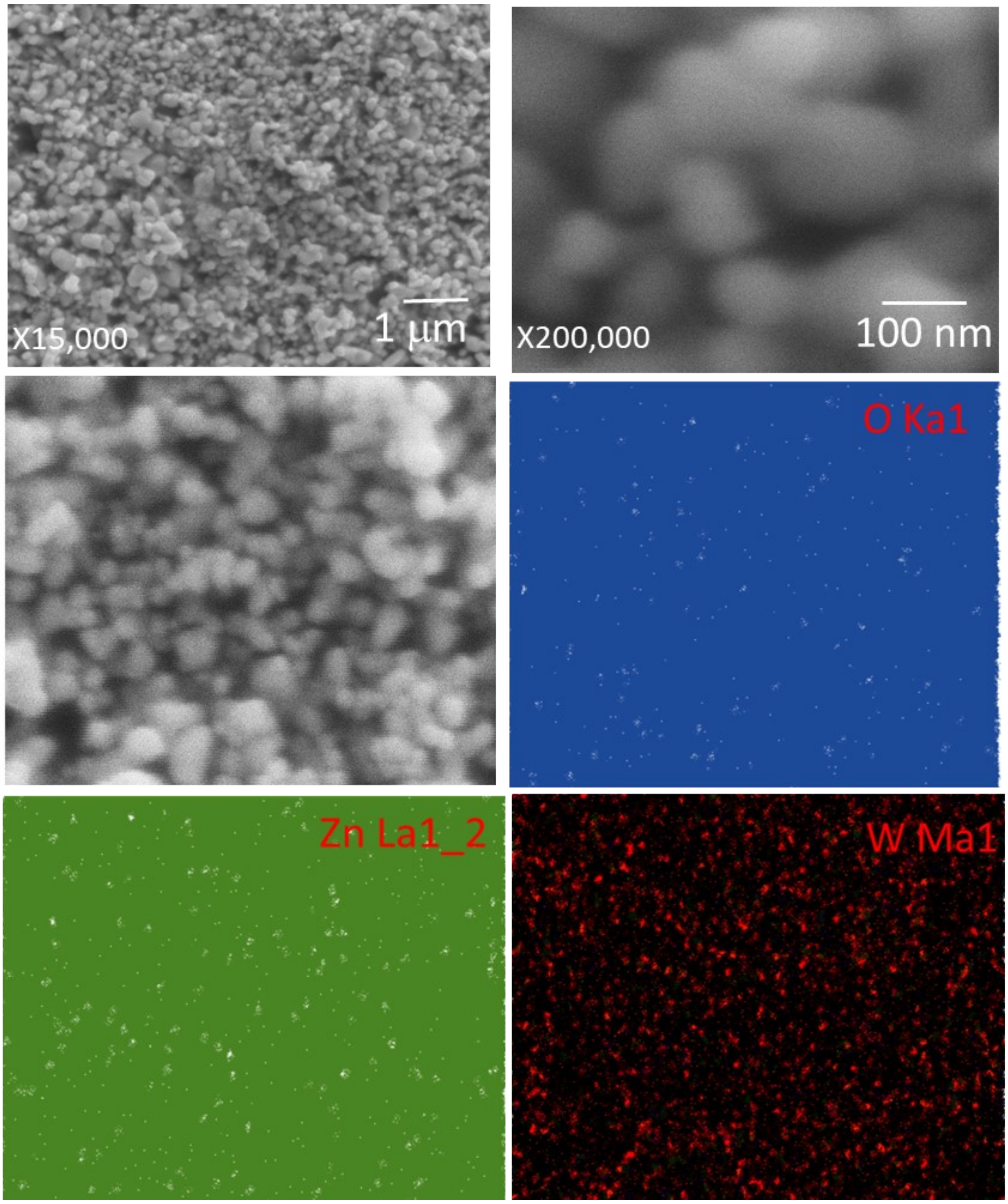


Fig. S6. Tungsten nanoparticles obtained from WO3+7Zn mixture at 800 ^{o}C for 2 hours.

5. MoO_3+30Mg system

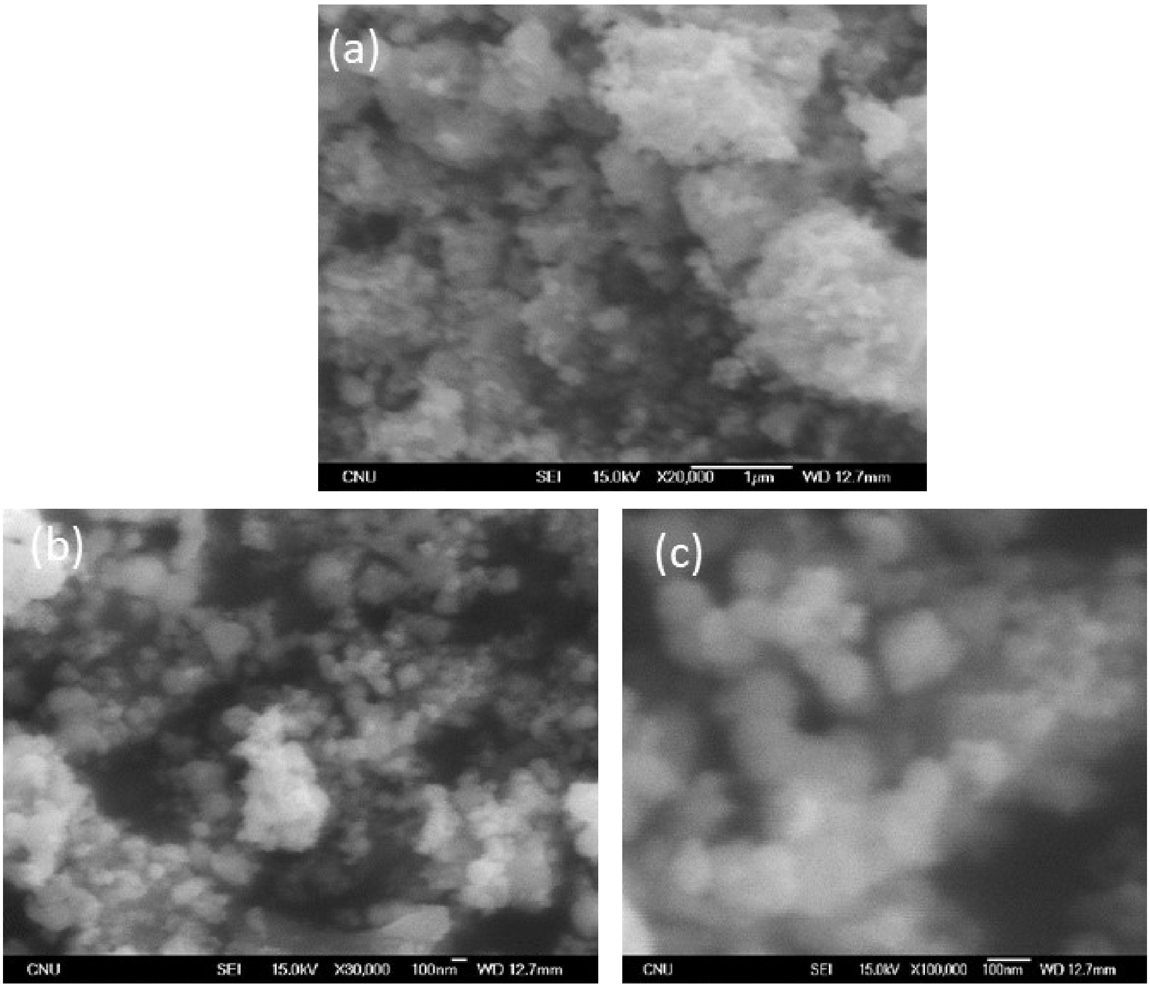


Fig. S7. SEM micrographs of Mo particles synthesized from MoO_3+30Mg mixture at 800 ^{o}C.

6. Catalytic test performance

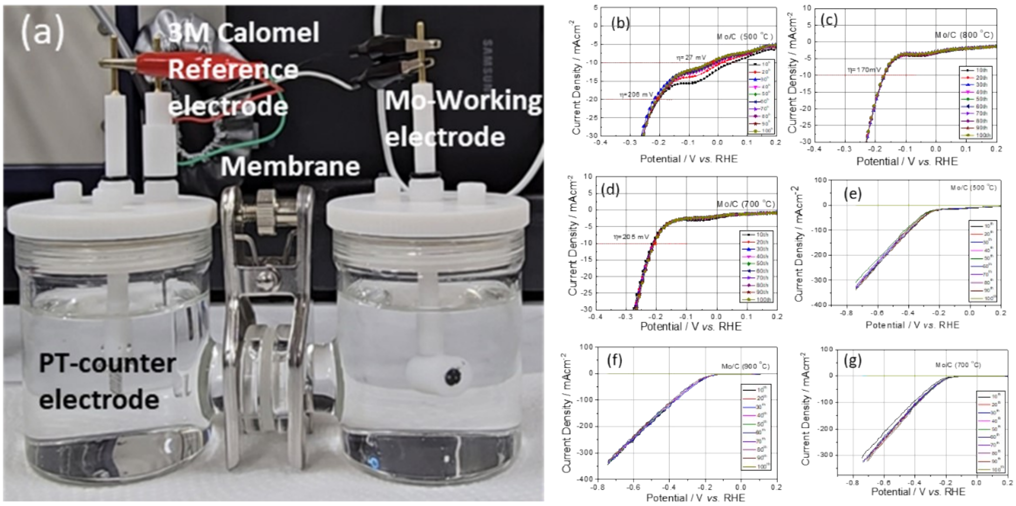


Fig. S8. (a) Three electrode systems for catalytic test performance. (b– g) Polarization curves for Mo-catalysts.

7. Polarization curves

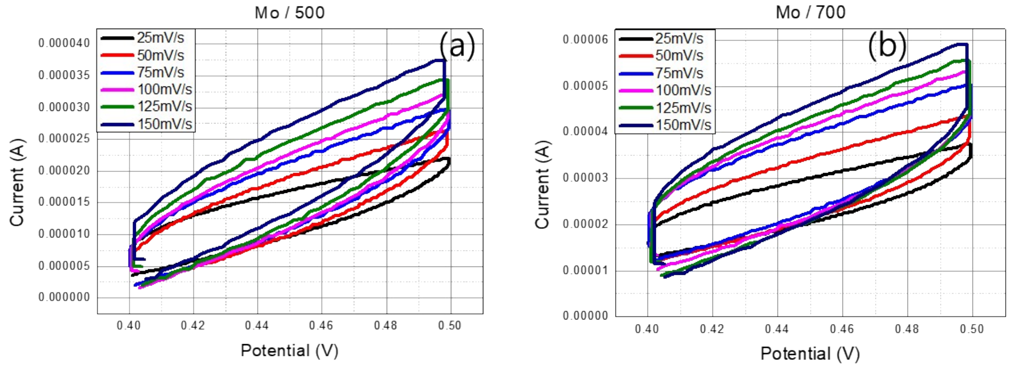


Fig. S9. Polarization curves with respect to scan rates: (a) Mo-500, (b) Mo-700.

8. Faradaic efficiency calculation

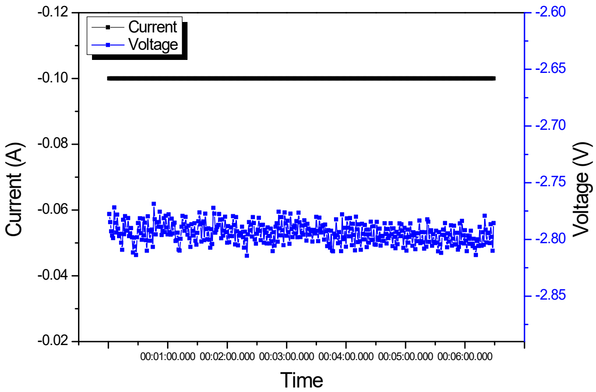
The following equation performed the Faradic Efficiency (FE) calculation:

$$\text{FE }(\%) = \frac{n_{actual}}{n_{theoretical}} * 100;$$

$$n_{\text{actual}} = \frac{PV}{RT}; \qquad n_{\text{theoretical}} = \frac{Q}{nxF};$$

8.1. Total charge calculation:

- Current (I) =100 mA = 0.1A
- Time (t) = 6 minutes 30 seconds = 390 seconds
- Volume of hydrogen gas (V) = 4 ml= 4×10^{-3} L
- Applied voltage: -2.77~2.82 V
- Q = 1×t = 0.1A×390s =39C



8.2. Hydrogen volume monitoring by experimental device;

Initial cylinder volume

Final cylinder volume

Total = 0.5mL * 8 = 4mL

Each division on the graduated cylinder represents 0.5 mL

Fig. S10. Experimental set-up for hydrogen volume measurement

8.3. *Actual amount of Hydrogen (n_{actual}):*

- P = 101325 Pa (standard atmospheric pressure)
- V = 4*10-3 L (volume of hydrogen)
- R = 8.314 J/(mol.K) (ideal gas constant)
- T=298K (room temperature)

n_{actual} = 101325×4×10^{-3}/8.314×298= 1.69×10^{-4} mol

8.4. *Theoretical amount of hydrogen ($n_{theoretical}$)*

- *n=2 (number of electrons to produce 1 mole of hydrogen)*
- *F=96485C/mol (Fraday's constant)*

$n_{theoretical}$ = 39 / 2 x 96485 = 2.02 x 10^{-4} mol

8.5. ***Faradaic Efficiency** = **1.69 x 10^{-4} mol / 2.02 x 10^{-4} mol x 100 = 83.7%***

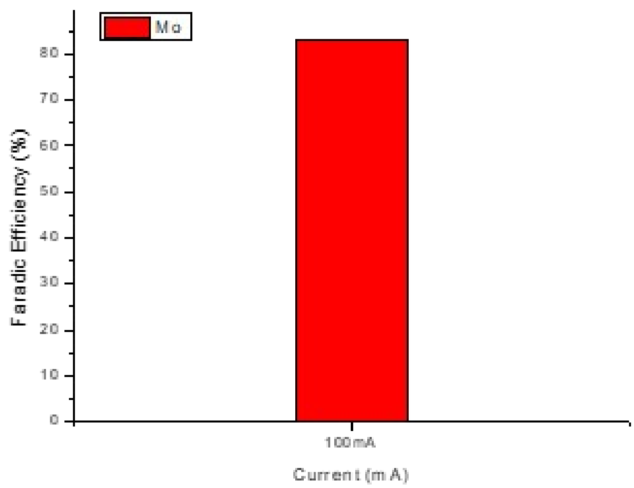


Fig. S11. Faradic efficiency