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Metal Doped Catalysts for Hydrogen Evolution Reaction

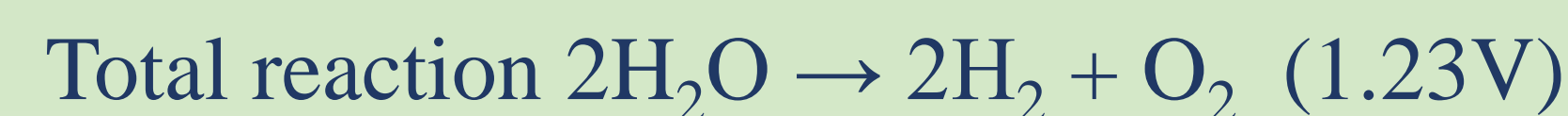
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Background and Purpose

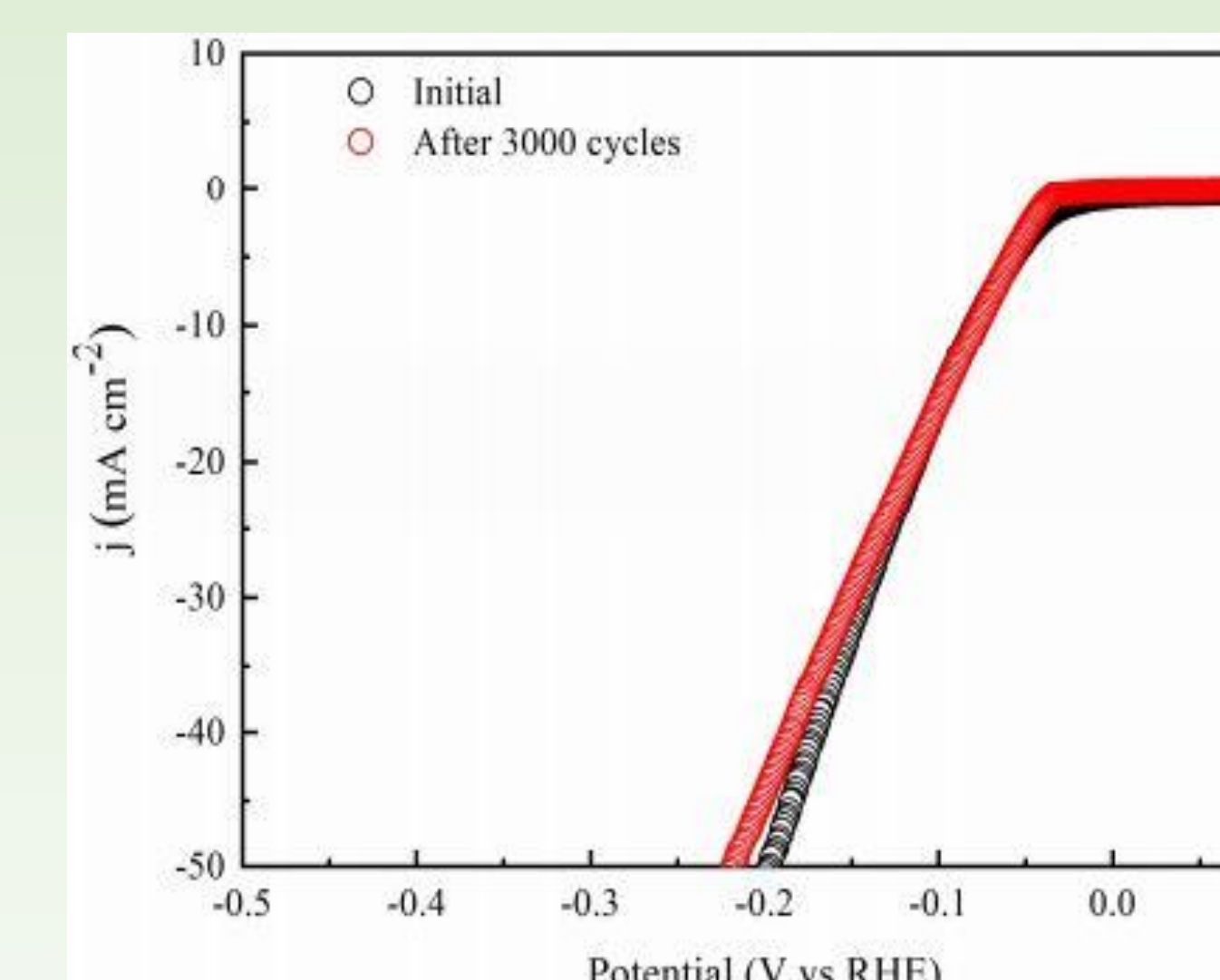
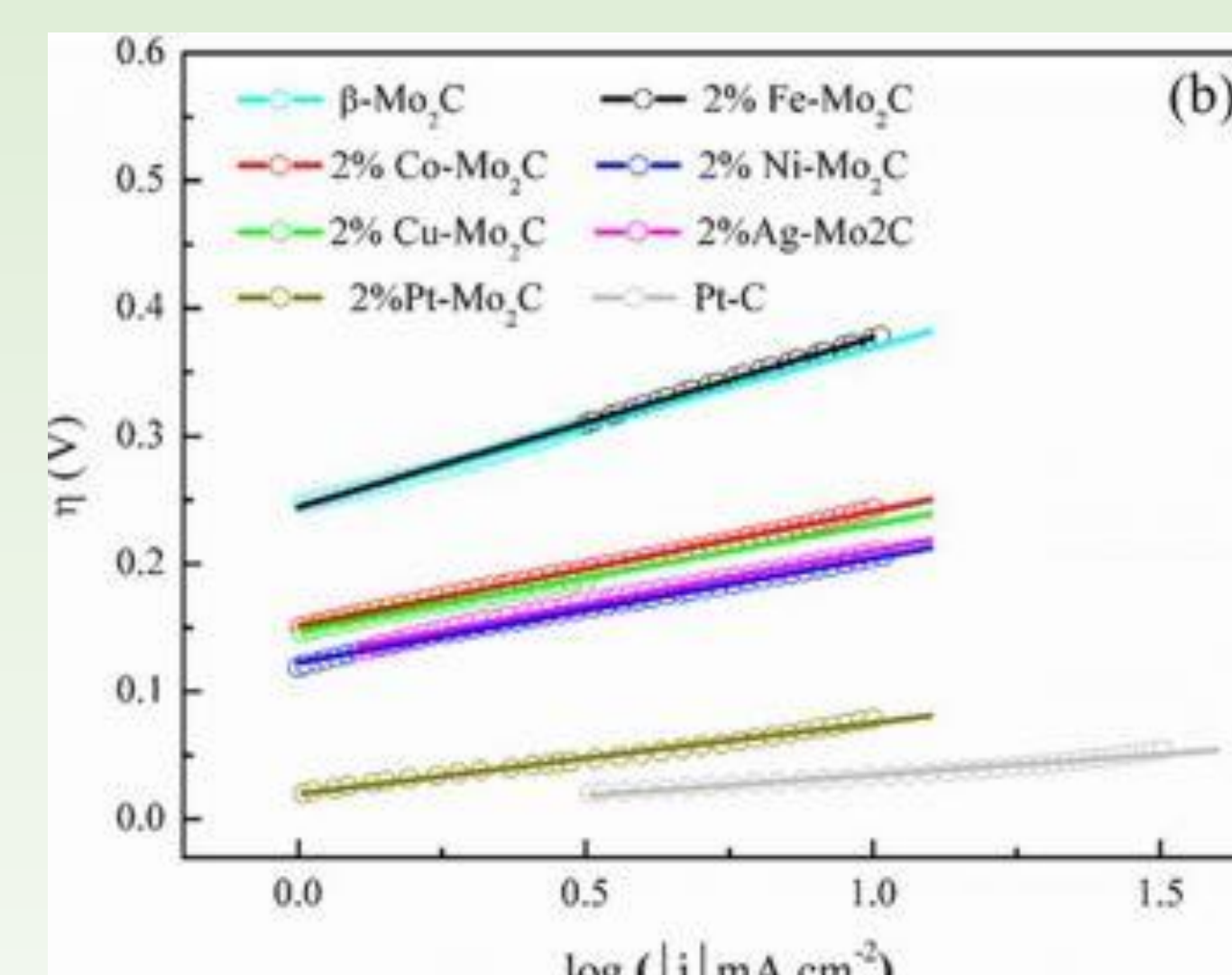
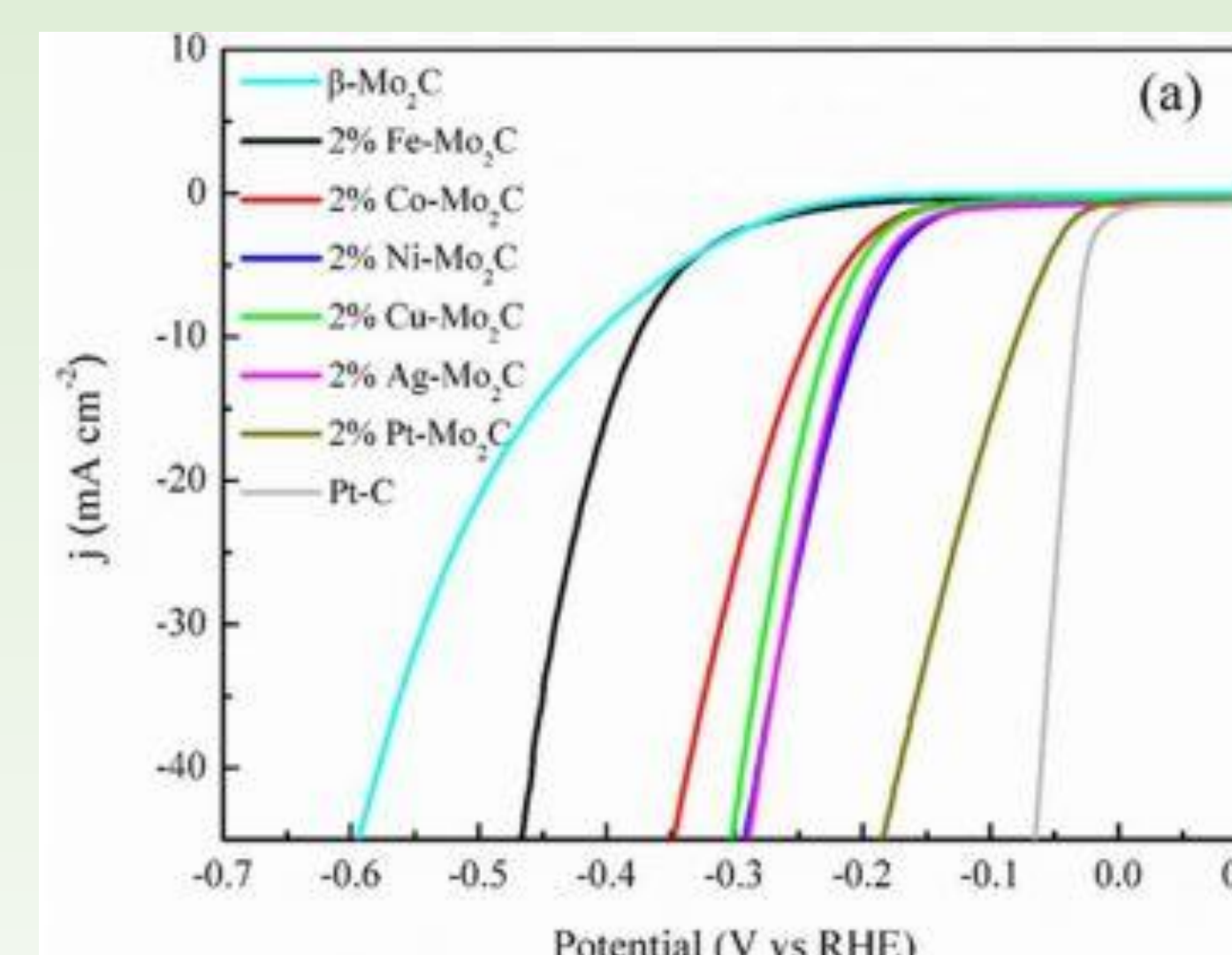
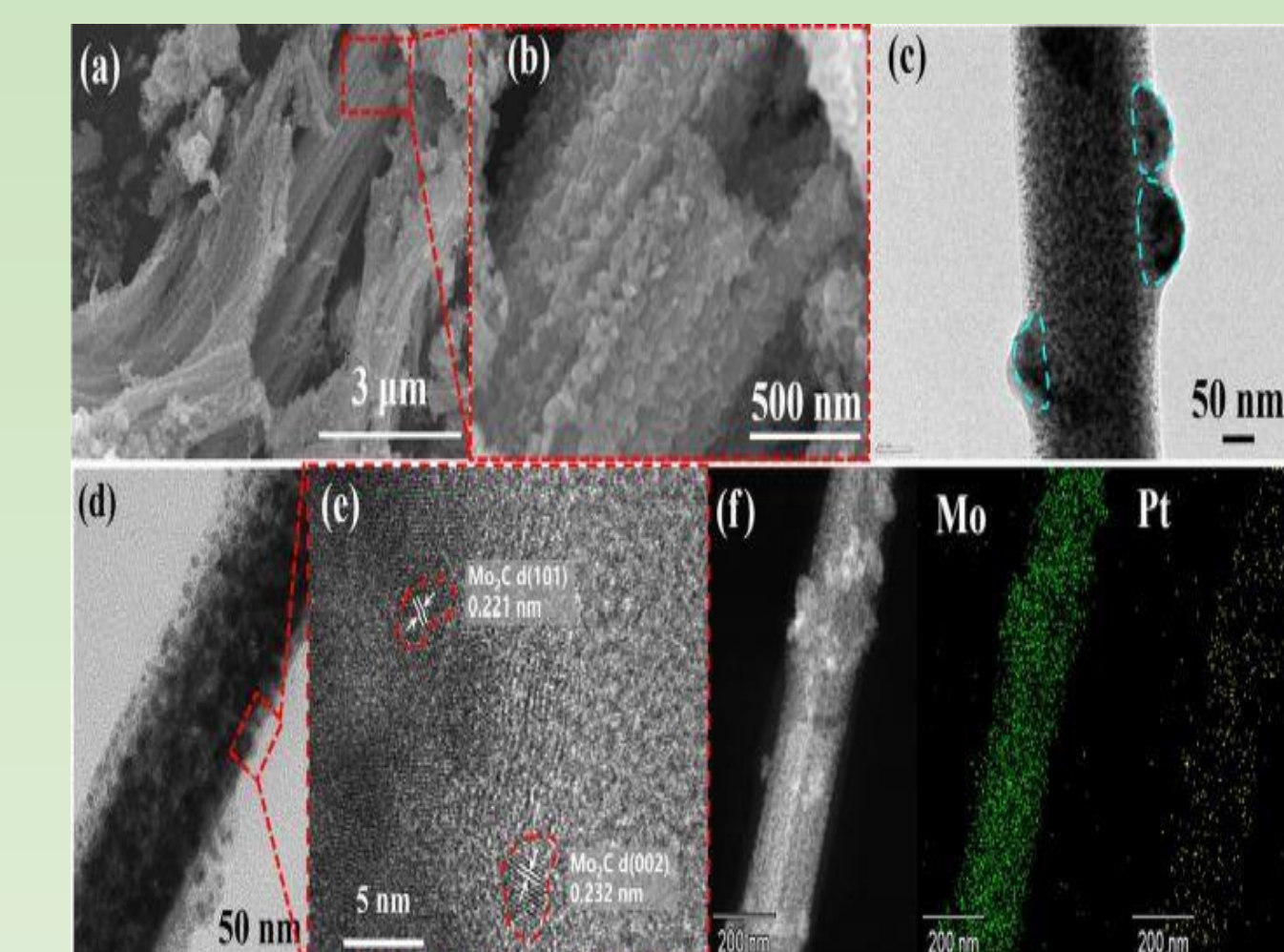
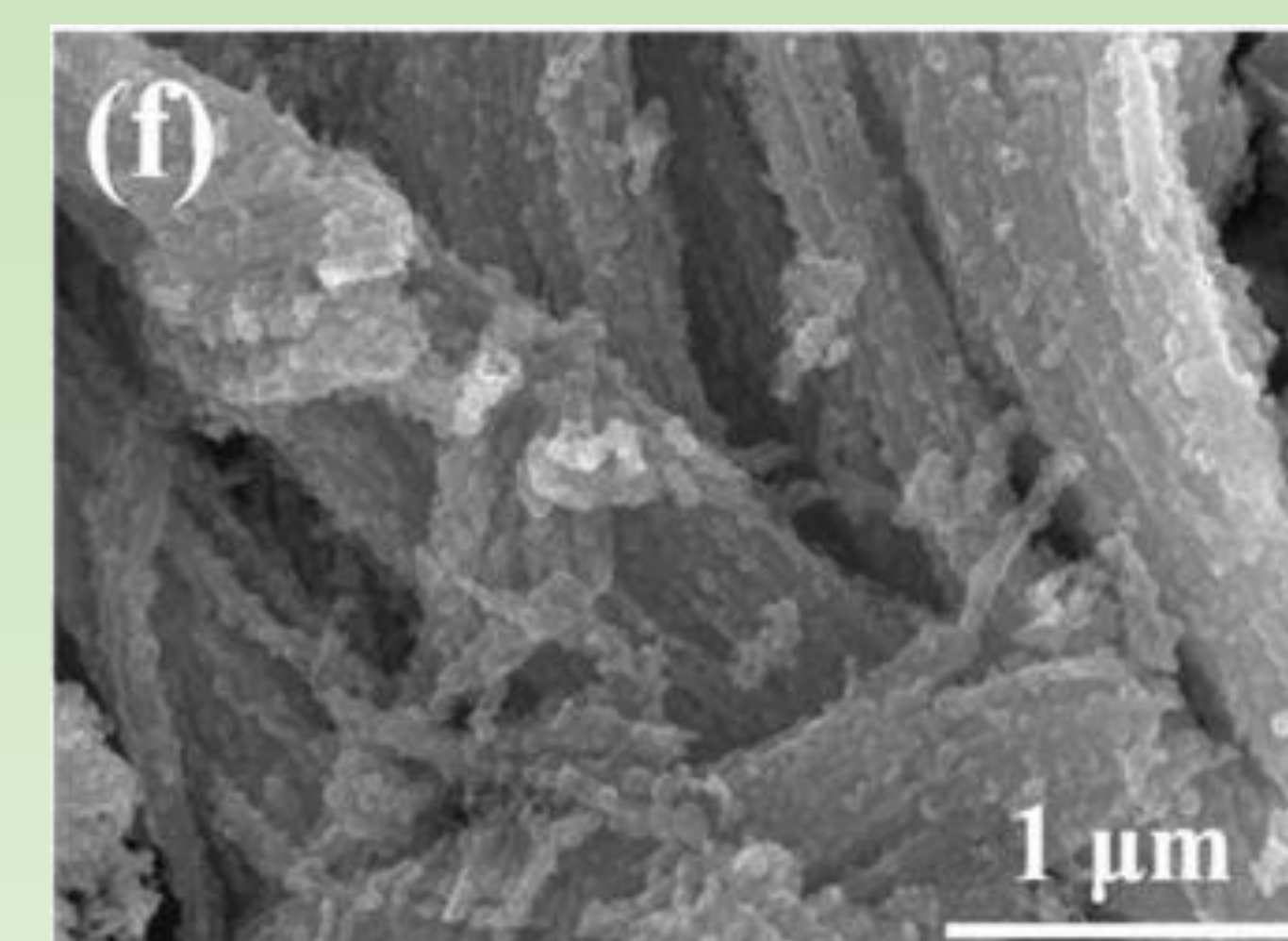
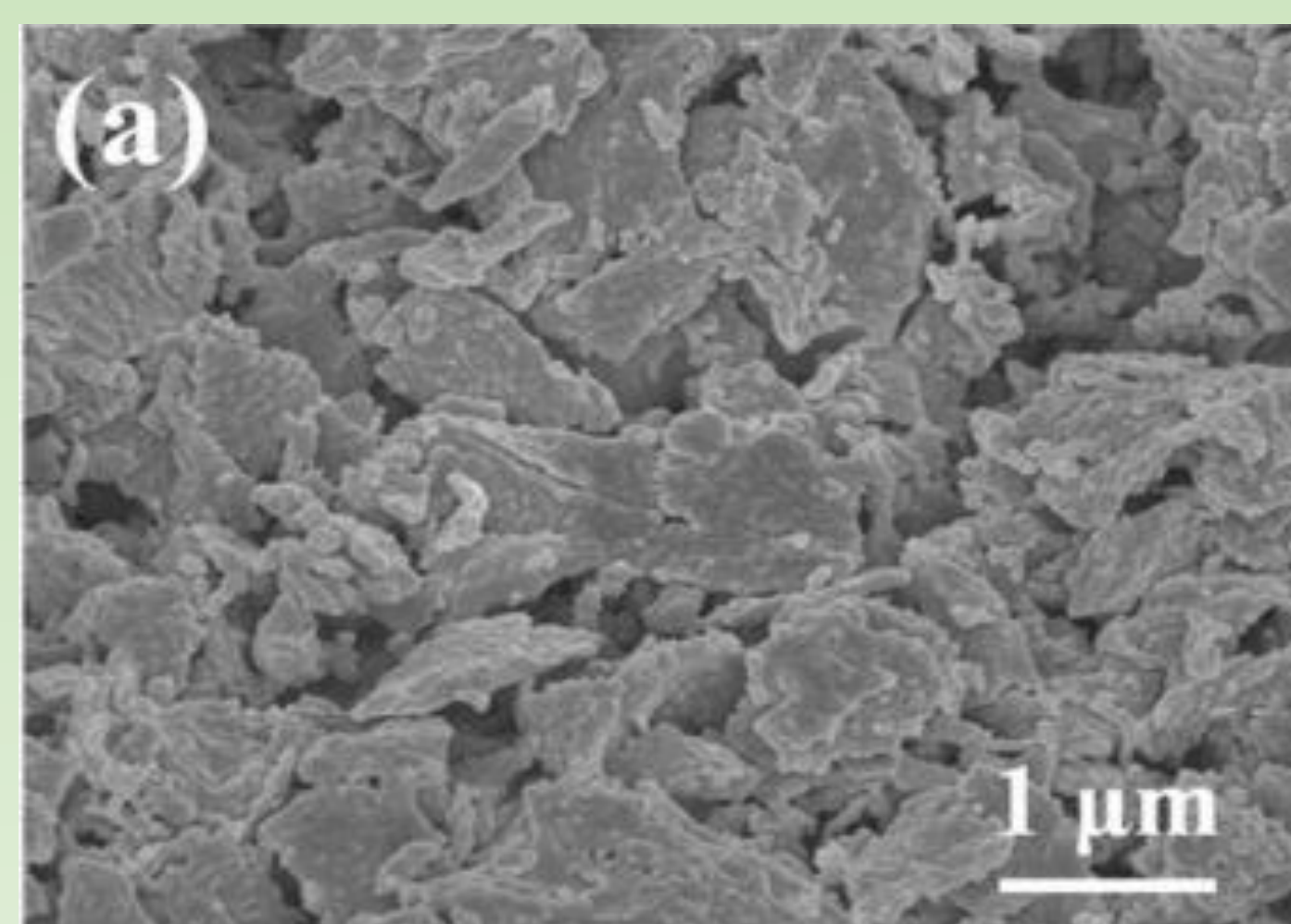
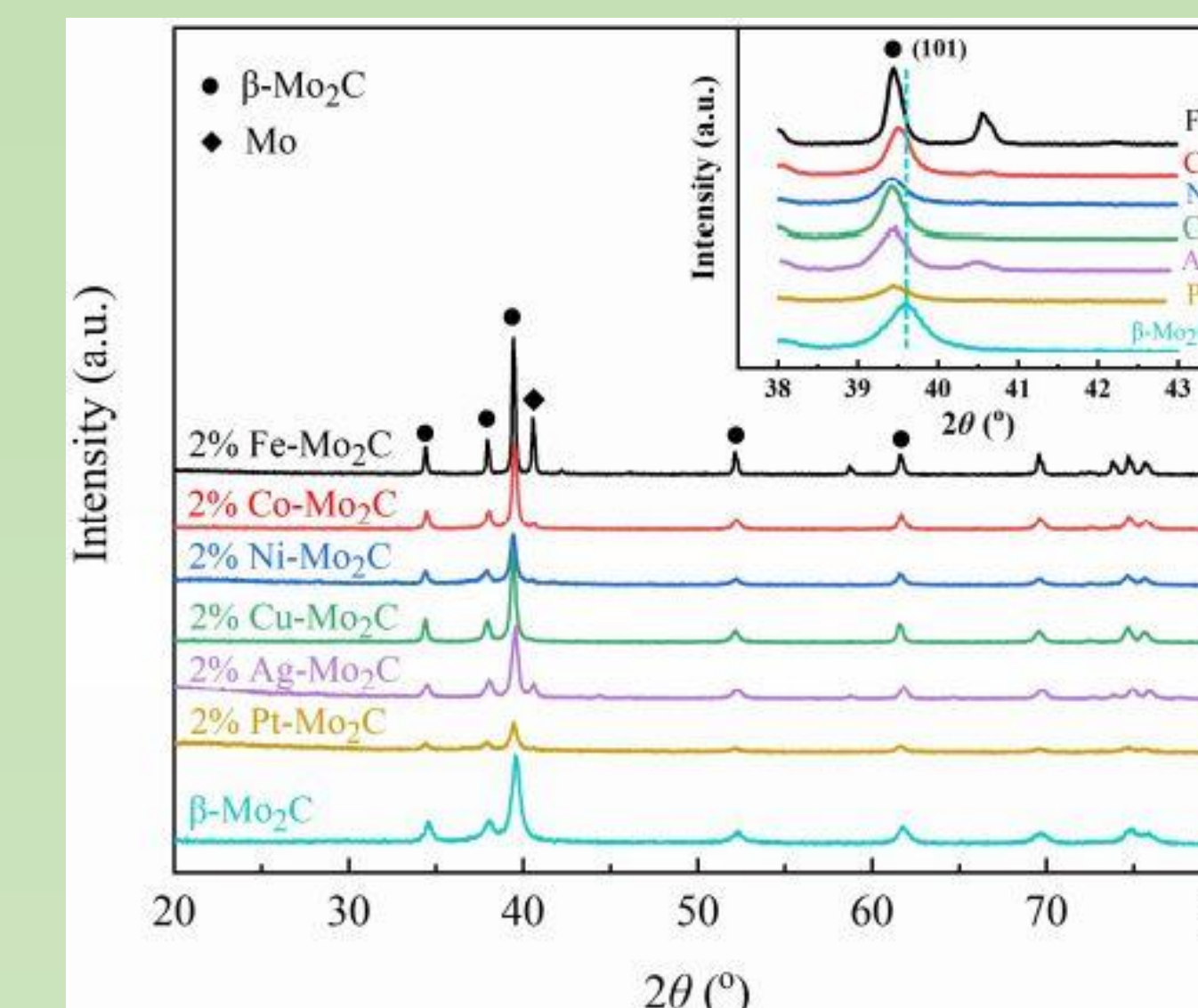
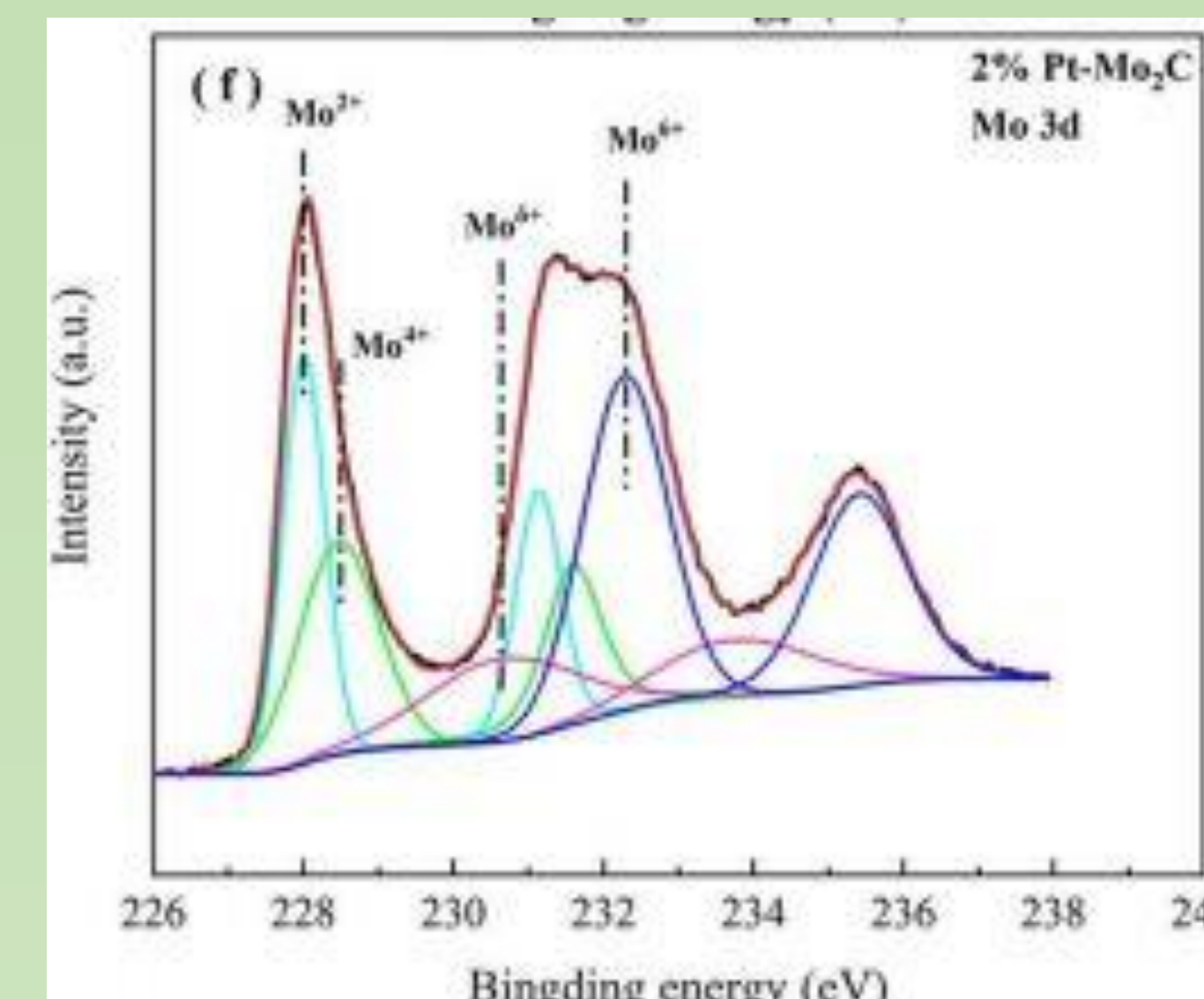
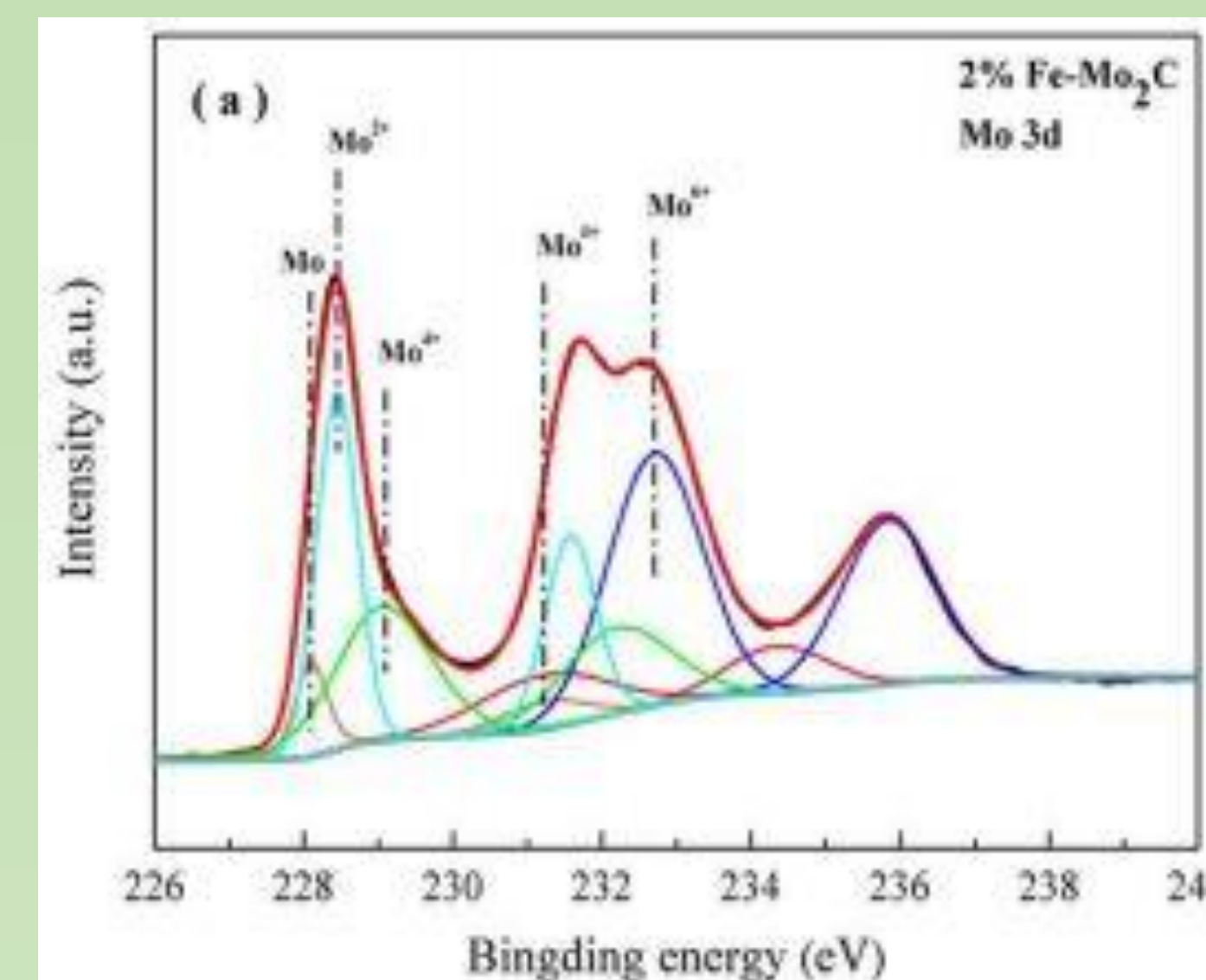
- ❖ The rapid depletion of fossil fuels and growing environmental concerns have created an enormous worldwide demand for alternative clean energy technologies.
- ❖ Hydrogen has a potential to be one of the most effective clean energy sources due to its high energy density of 141.86 MJ/kg and clean combustion.
- ❖ Water electrolysis via photochemical and photoelectrochemical are the promising pathways for sustainable hydrogen production.
- ❖ The water splitting reaction can be expressed chemically as:



Materials and Methods

- ❖ Ammonium heptamolybdate was dissolved in water followed by the introduction of the transition metal precursor.
- ❖ The molar ratio of M to M + Mo was 2%.
- ❖ Aniline was added dropwise followed by 1M HCl to adjust the pH between 2 and 4.
- ❖ The solution was heated in an oil bath to 50 C for 4 hours, washed with ethanol and water, then dried overnight at 50 C.
- ❖ Carburized of the samples occurred in a fixed-bed quartz micro-reactor at 800 C for 5 hours in an argon atmosphere.
- ❖ During the cool-down process, the samples were passivated in 1% O_2/Ar for 12 hours
- ❖ Final products were denoted as 2% M- Mo_2C (M: Fe, Co, Ni, Cu, Ag, and Pt).
- ❖ For comparison, the commercial HER catalyst 20% Pt/C was employed.
- ❖ Samples were loaded on glassy carbon electrode of 3 mm diameter.
- ❖ All electrochemical tests performed in 0.5M H_2SO_4 .
- ❖ All potentials are reported with reference to reversible hydrogen electrode + (0.198 + 0.059 pH) V.

Results



- ❖ X-ray diffraction peaks at 2θ of 34.8° , 38.4° , 39.8° , 52.5° , 61.9° , 69.6° and 74.9° are associated with β - Mo_2C . Fe, Co, and Ag doped Mo_2C displayed an additional peak at 2θ of 40.5° , indicative of metallic Mo. The peak at 2θ of 39.8° shifted to lower diffraction angles from the replacement of metal atoms.
- ❖ Mo 3d X-ray photoelectron spectroscopy for Ni, Cu, and Pt doped Mo_2C displayed 4 Mo species. Peaks with binding energy of 228.0-228.6 eV is from Mo^{2+} in Mo-C bonding. Mo^{2+} binding energy lowered when metal doped indicate enriched electron density. Metallic Mo was detected for Fe, Co, and Ag doped Mo_2C .
- ❖ Brunauer-Emmett-Teller analysis provided sharp decrease in surface area when doped with Fe or Co along with increased average pore size, while the Pt doped Mo_2C displayed a drastically increased surface area and decreased pore size.
- ❖ Scanning transmission electron microscopy showed that Fe doped Mo_2C had a random morphology while all other metal doped Mo_2C s had wire-like morphologies (diameter of 50-100 nm) composed of nanoparticles of 3-10 nm. There are small (100-200 nm) nanoparticles attacked on the Mo_2C wire surface.
- ❖ Polarization curves show that 2% Pt- Mo_2C had an overpotential of 79 mV and onset potential of 32 mV compared to the commercial 20% Pt/C overpotential of 34 mV and onset potential of 23 mV.

Conclusions

- ❖ The molybdenum oxides Mo^{4+} (MoO_2), Mo^{5+} (MoO_xC_y), and Mo^{6+} (MoO_3) were formed during the 12 hour passivation process.
- ❖ Lowered XPS binding energies of metal doped Mo_2C indicated the enriched electron density surrounding the molybdenum atom.
- ❖ Element mapping of 2% Pt- Mo_2C showed the uniform distribution of molybdenum and platinum throughout the nanowire.
- ❖ Metal doped molybdenum carbides showed higher electrocatalytic HER activity than pure molybdenum carbide
- ❖ The high catalytic performance of Pt doped Mo_2C was due to it high surface area, high uniform metal dispersion, increased number of exposed active sites, and enhanced electron transfer capability.
- ❖ Low tafel slopes around 80-90 mV/decade for Co, Ni, Cu, and Ag doped Mo_2C , and 55 mV/decade for Pt doped Mo_2C displayed that H_{ads} desorption is the rate-determining step in the two step reaction.
- ❖ Long term stability of Pt doped Mo_2C showed negligible difference between the polarization curves of the first and 3000th cycles.
- ❖ Low loading amount of 2% for Pt doped Mo_2C and high abundance of Molybdenum highlights application as a promising electrocatalyst replacement for commercial 20% Pt/C.

References

- ❖ Chen, Y., & Ma, Y., et al. (2018). Influence of Transition Metal on the Hydrogen Evolution Reaction over Nano-Molybdenum-Carbide Catalyst. *Catalysts*, 8,294.
- ❖ Vrabel, H., & Hu, X., et al. (2012). Molybdenum boride and carbide catalyze hydrogen evolution in both acidic and basic solutions. *Angew. Chem*, 124,12875.
- ❖ Ma, Y., et al. (2015). Embedded structure catalyst: A new perspective from noble metal supported on molybdenum carbide. *RSC Adv*, 5,15002.