



FACILE SYNTHESIS OF β - Mo_2C ELECTROCATALYST SUPPORTED ON MESOPOROUS CARBON FOR HYDROGEN GENERATION

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Abstract

Herein, we demonstrate a facile synthesis of β - Mo_2C embedded in mesoporous carbon support; Metal Organic Framework (MIL-53(Al)) was utilized as a novel source for mesoporous carbon support. Microscopic studies revealed the formation of monodisperse Mo_2C with <10 nm particle size homogeneously embedded in the porous carbon network. BET isotherms substantiated the mesoporous nature of carbon support with an average pore size of 3.8 nm. The electron diffraction, the HR-TEM, and the XRD analyses showed high degree of crystallinity with β -phase formation of Mo_2C , while XPS analysis revealed the different oxidation states of Mo (predominantly coordinated with carbon, and partially with oxygen). Electrocatalytic activity of as-synthesized samples were evaluated for hydrogen evolution reaction from alkaline water, and compared with that of $\text{Mo}_2\text{C}/\text{XC72}$ and commercial Pt/C catalysts.

Introduction

The surge in the field of renewable energy aiming to develop clean energy technology is continuing to rise. Quest for a H_2 -based economy derived from non-fossil resources remains at the forefront of future fuels. Electrocatalytic hydrogen generation via water electrolysis provides an important alternative to that extracted from hydrocarbon resources. Due to unique d-band electronic structure, Mo-based electrocatalyst such as, Mo_2C and MoS_2 has been the subject of intense investigation for HER reaction. Yet, functional and robust catalysts operating with reasonable current densities (J) at low overpotential in brine water are still scarce.

Materials & Methods

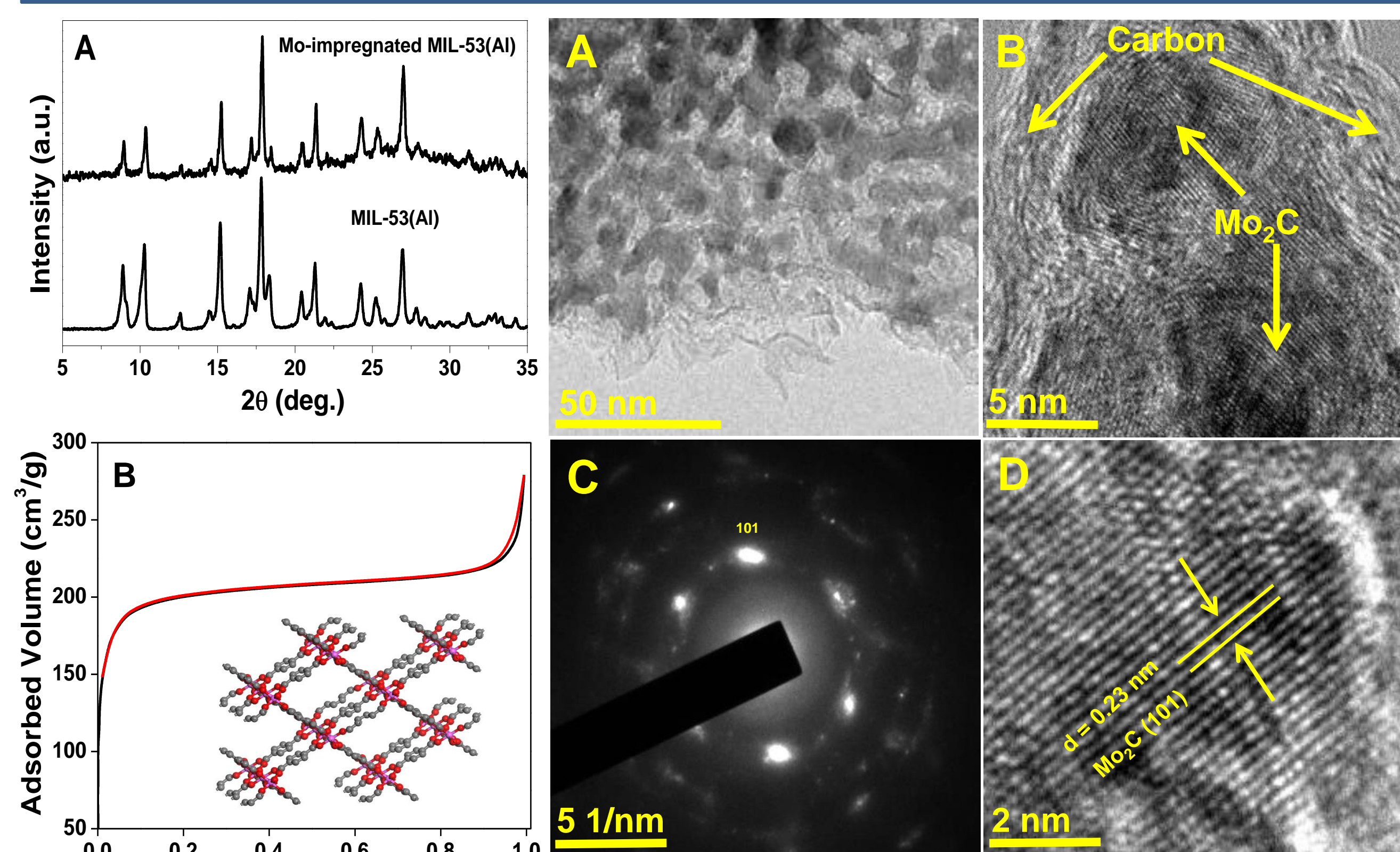
Synthesis of MOF MIL-53 (Al):

Al source, 1,4-benzenedicarboxylic acid and water were placed in a Teflon-lined steel autoclave and heated at 220 °C for specific time duration. After completion of reaction, the sample was filtered and washed with water.

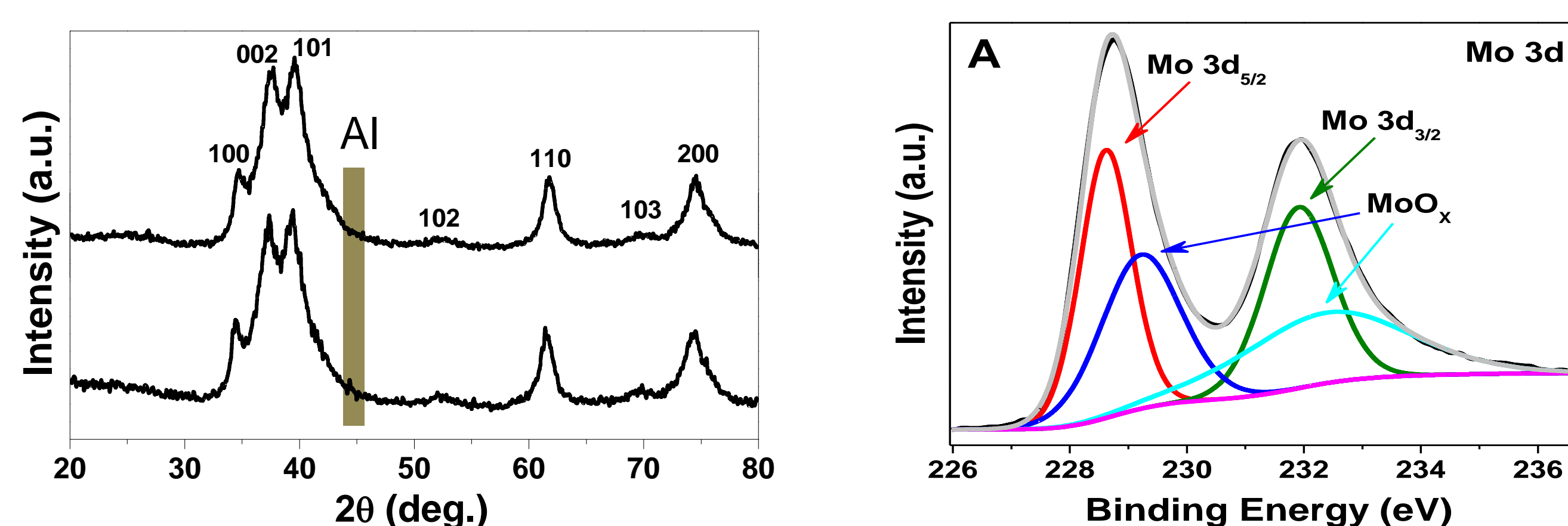
Synthesis of $\text{Mo}_2\text{C}/\text{C}$ porous composite:

A desired concentration of molybdenum source was dissolved in anhydrous isopropanol and the solution was kept under stirring. After complete dissolution of metal salt, a measured amount of MIL-53(Al) was suspended and kept under stirring for at least 12 h to ensure complete impregnation of Mo into the pores of MOF. Isopropanol was then evaporated under a vigorous stirring, leaving behind a gel-like material. The resulting material was dried and carburized in a tubular furnace in the presence of CH_4 at high temperature (≥ 750 °C). After reaction, the black product was collected and utilized as electrocatalyst for HER reaction. A homogeneous suspension consisting of Nafion and $\text{Mo}_2\text{C}/\text{C}$ was prepared and deposited on a glassy carbon electrode. The electrocatalytic activity was studied in a three-electrode cell.

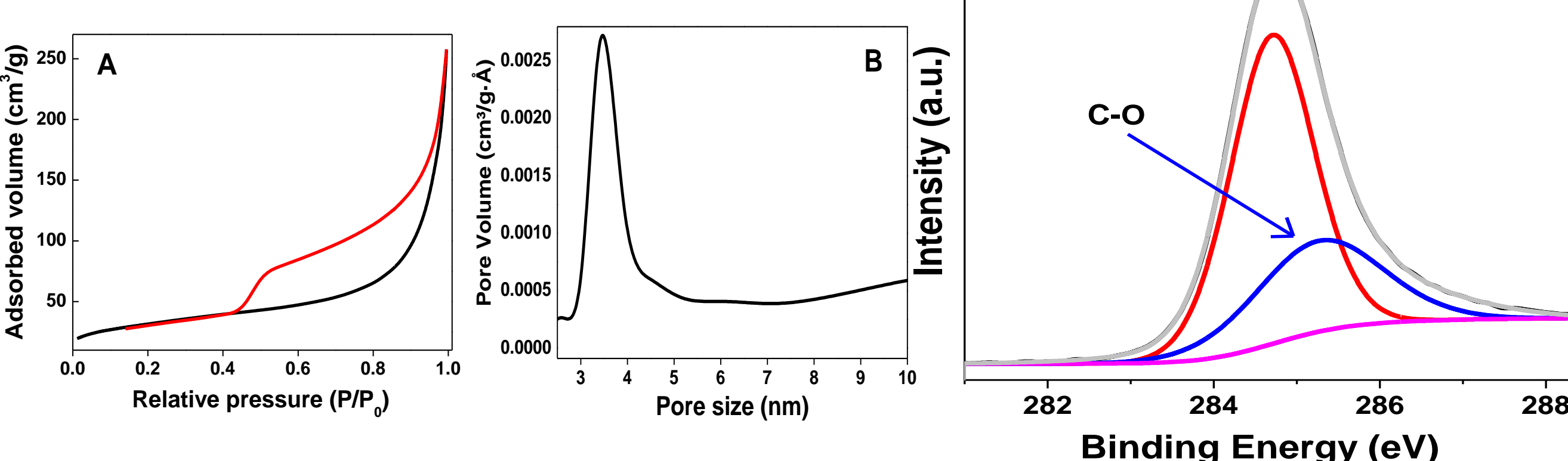
Results & Discussion



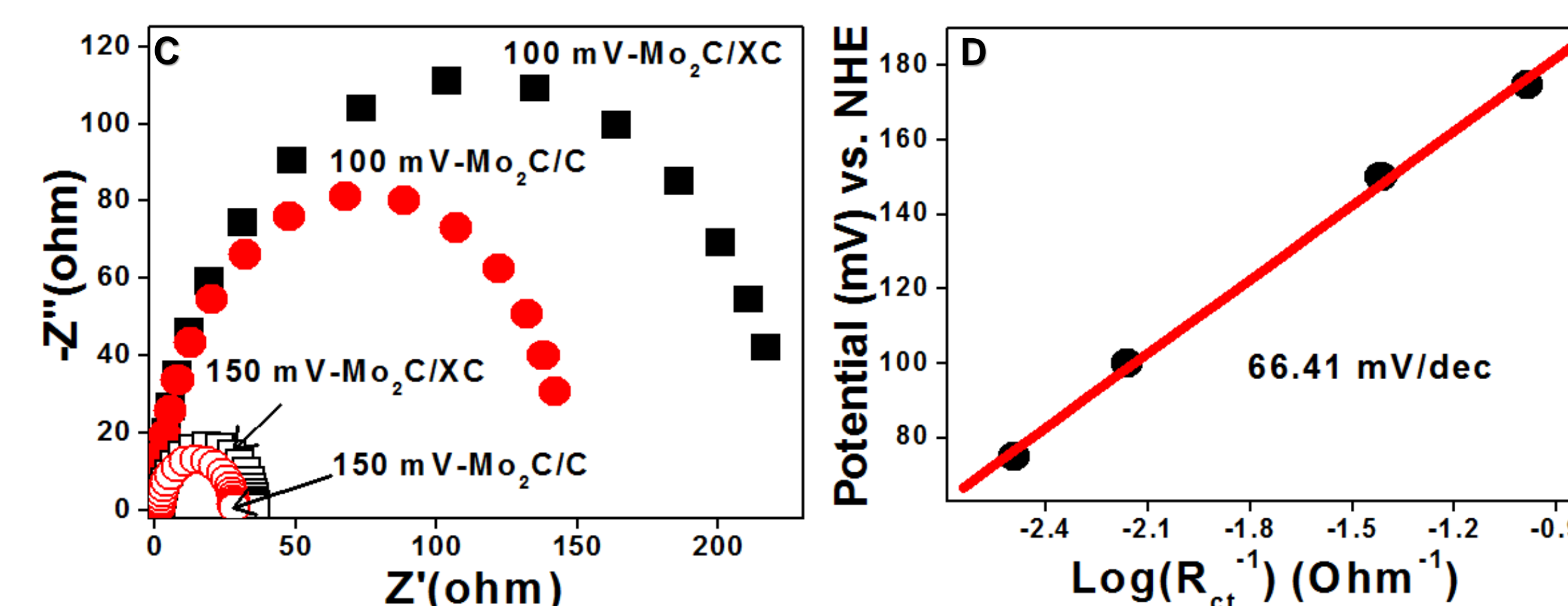
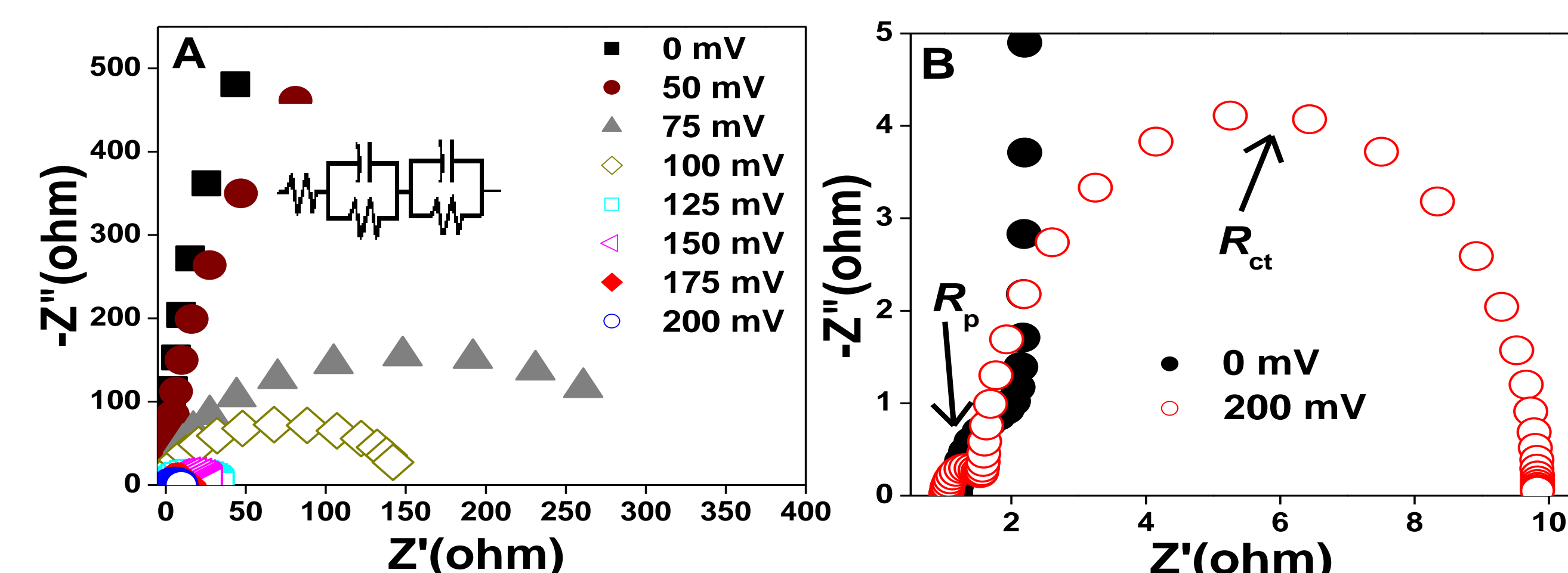
A - XRD of MIL-53(Al) before and after Mo impregnation, and (B) BET of MIL-53(Al).



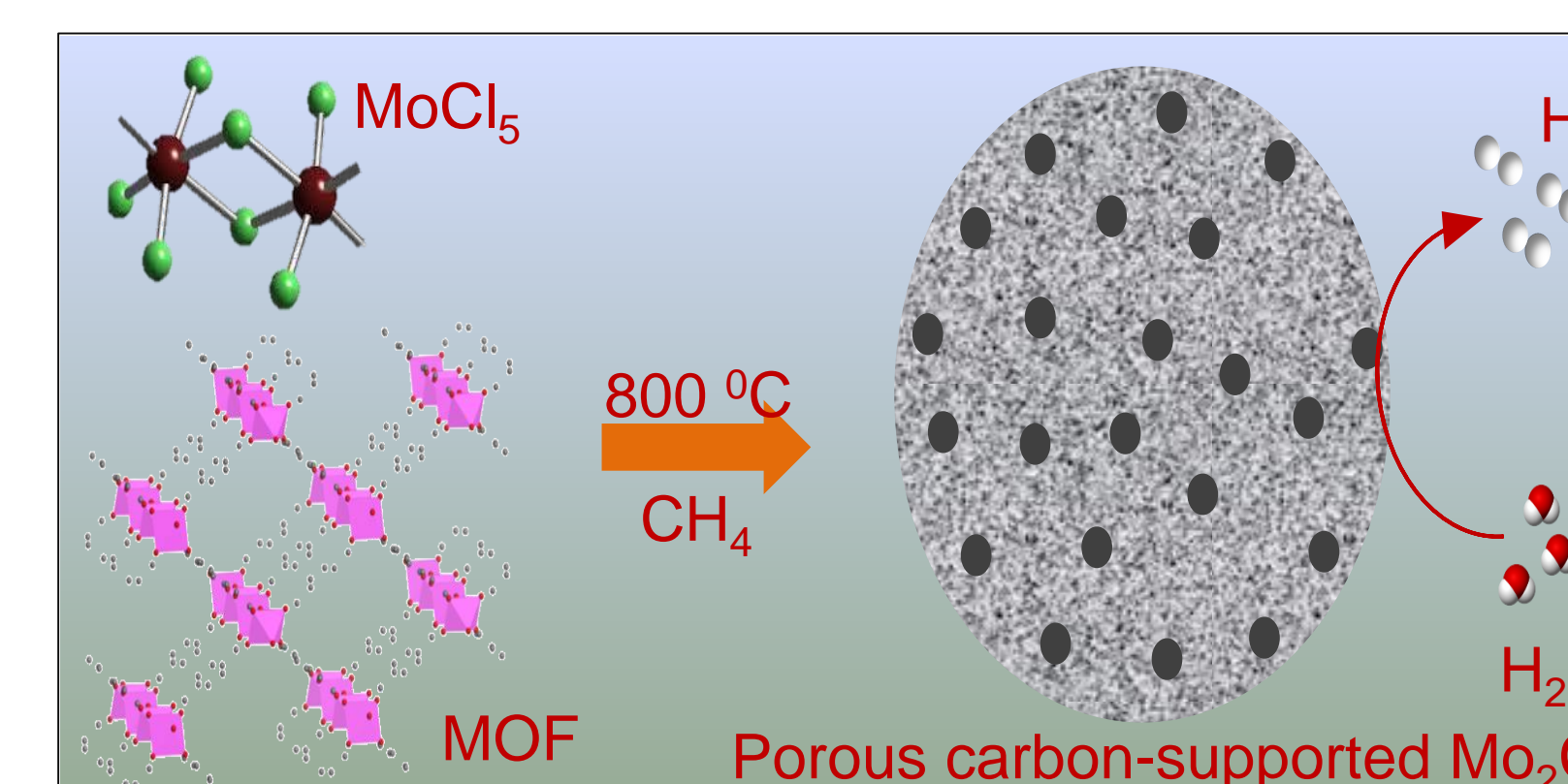
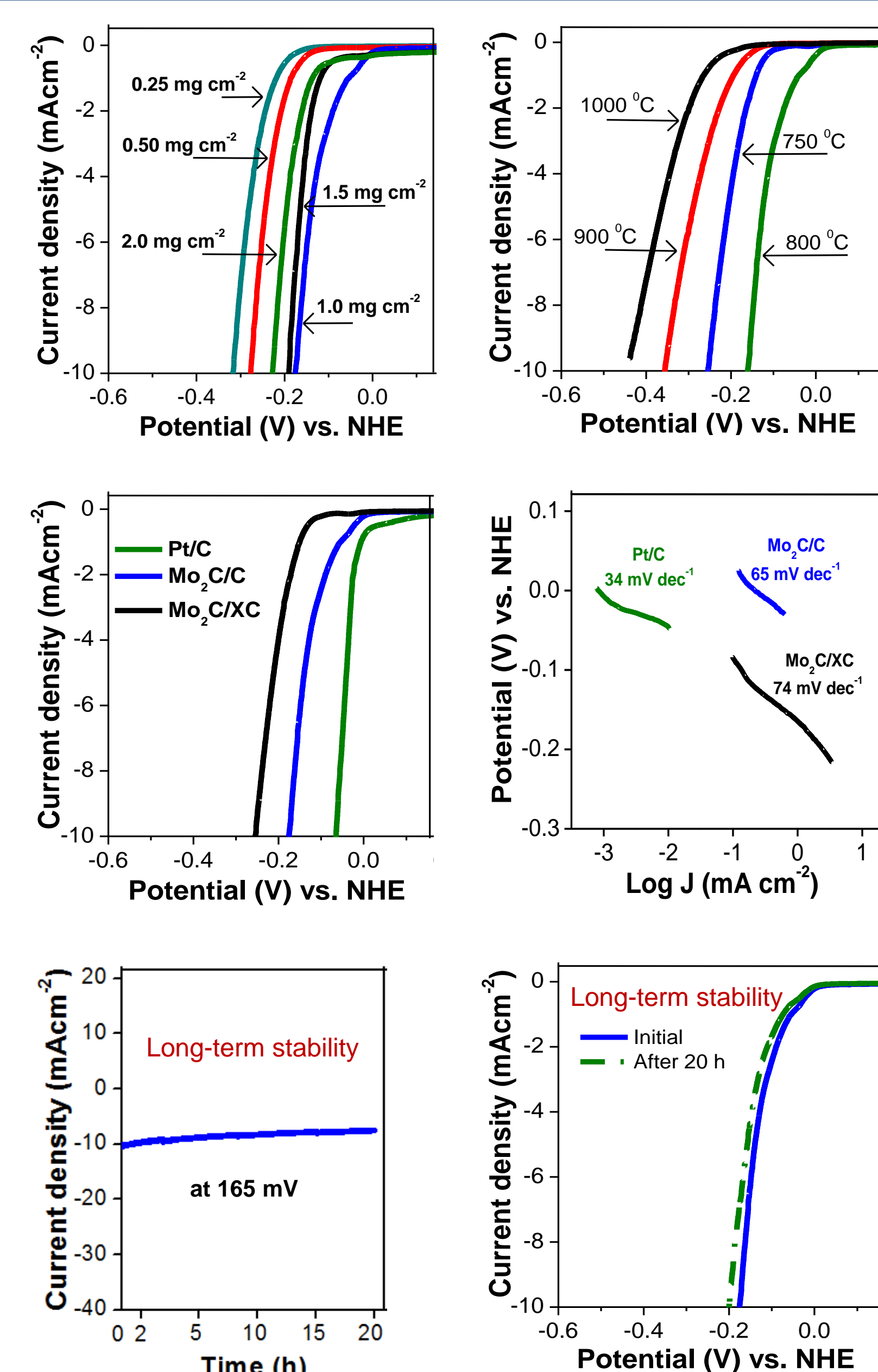
XRD of $\text{Mo}_2\text{C}/\text{C}$ before and after Al removal



BET isotherms (A), and pore size distribution (B) of $\text{Mo}_2\text{C}/\text{C}$.



Nyquist plots recorded at different potential (vs. NHE) (A), Nyquist plots with enlarged region showing two semicircles (B), comparative Nyquist plots of $\text{Mo}_2\text{C}/\text{C}$ and $\text{Mo}_2\text{C}/\text{XC}$ at $\eta = 100$ mV and 150 mV (C), and Tafel plot (D).



Conclusions

- Demonstrated a novel strategy to fabricate β - $\text{Mo}_2\text{C}/\text{C}$ electrocatalyst for H_2 evolution reaction from alkaline water.
- Metal Organic Framework namely MIL-53(Al) rendered (1) confined environment for the nucleation and growth of fine Mo_2C nanoparticles, and (2) porous and rigid support for Mo_2C nanoparticles.
- Restricted space of MIL 53(Al) in the form of porous texture seemed to inhibit agglomeration and coalescence of in situ-developed Mo_2C , presumably through homogeneous distribution of Mo ions inside/outside the pores, and thus guided the in situ formation of fine and fairly dispersed Mo_2C nanocrystallites in carbon texture.
- Electrocatalytic performance of as-prepared $\text{Mo}_2\text{C}/\text{C}$ was found to be stable, better than that of $\text{Mo}_2\text{C}/\text{XC72}$, and close to commercial electrocatalyst Pt/C.
- Electrochemical impedance analysis of $\text{Mo}_2\text{C}/\text{C}$ suggested the presence of two-time constants and the improved electrocatalytic performance of $\text{Mo}_2\text{C}/\text{C}$ was attributed to faster charge kinetics. Furthermore, Tafel slope suggested that a Volmer–Heyrovsky mechanism was operative in the HER reaction.

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FURTHER INFORMATION

M. Qamar, A. Adam, B. Merzougui, A. Helal, O. Abdulhamida, M. N. Siddiqui, *Journal of Material Chemistry A*, 4, (2016) 16225-16232.

References

1. Q. Lu, G. S. Hutchings, W. Yu, Y. Zhou, R. V. Forest, R. Tao, J. Rosen, B. T. Yonemoto, Z. Cao, H. Zheng, J. Q. Xiao, F. Jiao and J. G. Chen, *Nat. Commun.*, 2015, 6, 6567–6574.
2. M. S. Fabera and S. Jin, *Energy Environ. Sci.*, 2014, 7, 3519–3542.
3. P. Xiao, W. Chen and X. Wang, *Adv. Energy Mater.*, 2015, 5, 1500985–1500997.
4. P. C. K. Vesborg, B. Seger and I. Chorkendorff, *J. Phys. Chem. Lett.*, 2015, 6, 951–957.
5. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Marković, *Science*, 2007, 315(5811), 493–497.