Chem Catalysis

CellPress

Preview

Carbonitride MXenes: An innovative catalyst support for sustainable hydrogen production

Kenneth J. Gordon,[1] Xiao-Dong Zhou,[1,*] and Ling Fei[1,*]

In this issue of Chem Catalysis, Djire's research team at Texas A&M University employed Ti_3CN as catalyst support for Ru nanoparticles in the hydrogen evolution reaction (HER). The catalyst exhibited excellent performance, comparable to noble-metal catalysts. These findings underscore the substantial potential of MXenes as catalyst supports for various electrochemical catalysis.

The urgency for sustainable and economical replacements for fossil fuels as energy sources has become more pressing with growing concerns about climate change and greenhouse gases. Hydrogen has emerged as a potential replacement; however, the challenge of producing hydrogen in a sustainable manner remains.[1–3] The main hydrogen production comes from steam reforming and coal gasification, both of which are based on fossil fuels.[3] While electrocatalytic water splitting using the HER is a cleaner method, it requires a catalyst to accelerate the reaction to a viable rate.[1–4]

One major challenge in hydrogen production through electrocatalytic water splitting is the high cost and low abundance of platinum (Pt), the state-of-the-art catalyst.[2–4] To address this, ruthenium (Ru) is a promising alternative due to its similar bond strength with hydrogen and lower cost.[3,5] However, the cost is still relatively high. To mitigate this, researchers are exploring methods to optimize the distribution of nanoparticles/atoms on a catalyst support to minimize the amount of metal while maximizing the number of active sites.[6]

Compared to bulk materials, a catalyst comprised of metal atoms or nanoparticles offers better active-site utilization and potentially reduces metal usage. The challenge is to eliminate the agglomeration that often occurs during synthesis and catalyst operation.[6–8] To address this, a suitable catalyst support that provides strong interactions between the metal atoms/nanoparticles and the substrate is crucial.[6,7] The ideal support must prevent agglomeration, have high conductivity, be highly electrochemically active, and possess good hydrophilicity. While various support materials have been explored, such as metals, metal sulfides, metal oxides, carbon nanotubes, graphene, and other carbon-based materials, they tend to lack one or more of the necessary characteristics.[7] MXenes, on the other hand, have been identified as a potential support material that meets all these criteria.

MXenes are a group of two-dimensional metal carbides, nitrides, and carbonitride materials that are produced by etching off the "A" layers (generally Al) of MAX ($M_{n+1}AX_n$) phases, where M is a transition metal; A is a IIIA or IVA element; and X is carbon and/or nitrogen.[4] This A-layer etching process leads to the immediate functionalization of exposed metal atoms with surface terminations such as O, OH, and F, resulting in MXenes with a general formula of $M_{n+1}X_nT_x$, where T_x represents the surface termination (O, OH, and/or F).[4,5]

The unique properties of MXenes, including high electrical conductivity, large surface area, and excellent hydrophilicity, position them as a highly promising support material for catalytically active metal nanoparticles or atoms.[4,9] It has also been demonstrated that nonmetallic heteroatom doping is a promising functionalization strategy for enhancing the performance of MXene nanosheets as catalyst support. By introducing nonmetallic elements as heteroatoms into the MXene structure, it is possible to modify the electronic properties and surface chemistry, thereby further promoting the catalytic reaction. Liu et al. demonstrated the use of stabilized Ru atoms on nitrogen-doped Ti_3C_2 MXene (Ru-N-Ti_3C_2), achieving lower overpotential compared to non-heteroatom anchored Ru-Ti_3C_2.[7] Similarly, stabilized Ru nanoparticles on boron-doped Ti_3C_2 (Ru-B-Ti_3C_2) were successfully synthesized, which exhibited a lower overpotential compared to non-doped Ru-Ti_3C_2.[5] It is worth noting that the synthesis of such catalysts often involves an additional step of heteroatom doping, which may increase the overall cost.

A recent study published in Chem Catalysis by Djire's group proposed Ti_3CN, an alternative MXene material, as a support for Ru metal nanoparticles for HER catalysis without the need for an additional heteroatom doping step.[10] To prepare the catalyst, the

[1]Department of Chemical Engineering, Institute for Materials Research and Innovation, University of Louisiana at Lafayette, Lafayette, LA 70504, USA

*Correspondence: xiao-dong.zhou@louisiana.edu (X.-D.Z.), ling.fei@louisiana.edu (L.F.)

https://doi.org/10.1016/j.checat.2023.100664

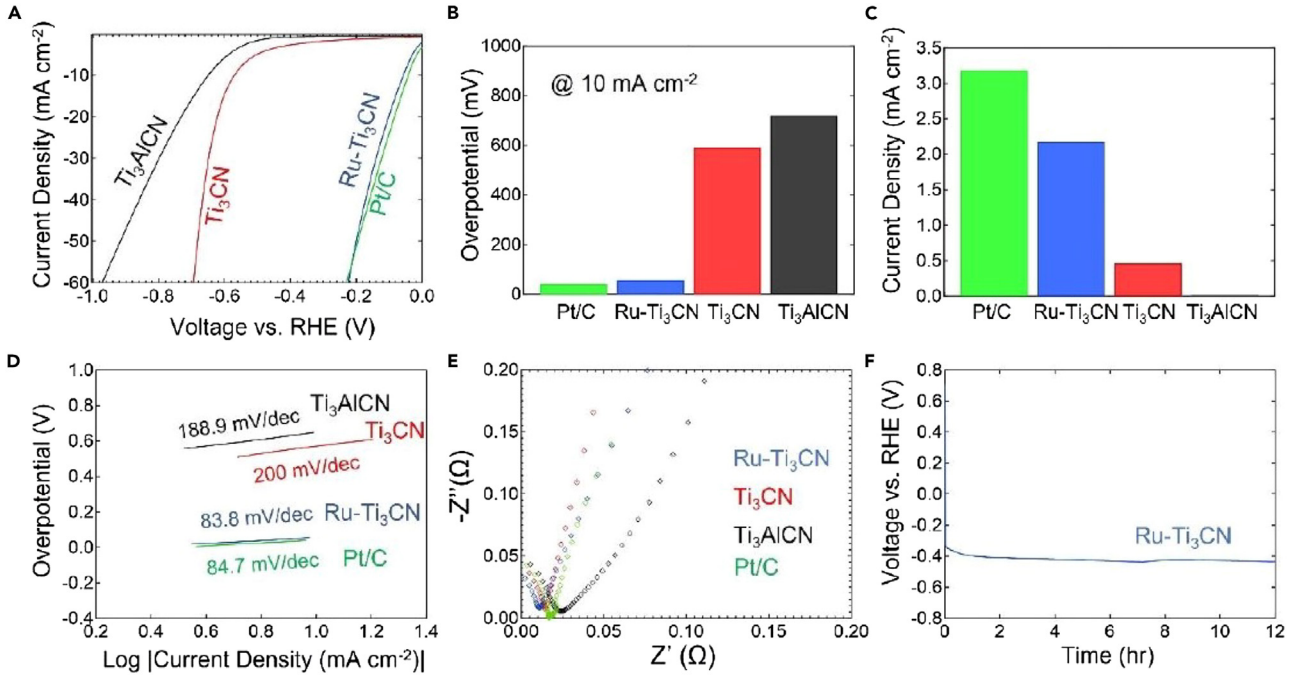

Figure 1. Electrochemical activity evaluation in 0.5 M KOH

(A) LSV scans.

(B) Overpotential at 10 mA cm^{-2}.

(C) Exchange current density.

(D) Tafel plot.

(E) Nyquist plot of Ti_3AlCN, Ti_3CN, Ru-Ti_3CN, and Pt/C in 0.5M KOH.

(F) Chronopotentiometry plot of Ru-Ti_3CN in 0.5M KOH. LSVs were recorded at 5 mV s^{-1} and 1600 RPM.[10]

researchers first etched Ti_3AlCN to obtain Ti_3CN and then reduced $RuCl_3$ using $NaBH_4$ to form Ru nanoparticles on the Ti_3CN support. The as-synthesized catalyst was obtained through filtration and drying. Density Functional Theory (DFT) calculations showed that Ru preferentially binds to the MXene surface, acting as active sites, rather than substituting the titanium atoms. This resulted in a remarkable synergistic effect between Ru and Ti_3CN in catalyzing the HER process. Notably, the catalyst exhibited excellent performance, with a low overpotential of 56 mV at 10 mA cm^{-2} in an alkaline electrolyte, rivaling both their carbide counterpart (Ru-Ti_3C_2) and heteroatom-doped Ru-X-Ti_3C_2, as well as performing comparably to noble-metal catalysts (*e.g.*, Pt/C). The performance of Ru-Ti_3CN shown in Figure 1 closely matches that of Pt on carbon. This result highlights the potential of using MXene supports as a new approach to develop cost-effective and efficient catalysts.

This preview highlights a promising approach toward the cost-effective and sustainable production of green hydrogen, offering a viable and less-expensive alternative to platinum on carbon catalysts without compromising the electrolysis performance. The straightforward synthesis process suggests the possibility of scalable production. As a class of catalyst support, MXenes present a wide range of possibilities for further exploration and diversification. This perspective lays a solid foundation for investigating other types of MXenes with a potential for even higher performance. Another promising avenue for future research is to identify and evaluate non-precious metals, such as transitional metals, on MXene supports, which can be more cost-effective. This exploration could lead to the development of high-performance catalysts that are both efficient and economically viable. Furthermore, MXene-based catalyst supports hold significant potential for various electrochemical catalysis applications beyond hydrogen production.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under NSF-2223447 and NSF-2119688.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Zhang, J., Zhao, Y., Guo, X., Chen, C., Dong, C.L., Liu, R.S., Han, C.P., Li, Y., Gogotsi, Y.,

and Wang, G. (2018). Single platinum atoms Immobilized on an MXene as an efficient catalyst for the hydrogen evolution reaction. Nat. Catal. *1*, 985–992. https://doi.org/10.1038/s41929-018-0195-1.

2. Kang, Z., Chen, Y., Wang, H., Alia, S.M., Pivovar, B.S., and Bender, G. (2022). Discovering and demonstrating a Novel high-Performing 2D-Patterned Electrode for Proton-Exchange Membrane water electrolysis Devices. ACS Appl. Mater. Interfaces *14*, 2335–2342. https://doi.org/10.1021/acsami.1c20525.

3. Yang, Y., Yu, Y., Li, J., Chen, Q., Du, Y., Rao, P., Li, R., Jia, C., Kang, Z., Deng, P., et al. (2021). Engineering ruthenium-based Electrocatalysts for effective hydrogen evolution reaction. Nano-Micro Letters, *1* (Springer Science and Business Media B.V. December). https://doi.org/10.1007/s40820-021-00679-3.

4. Jiang, Y., Sun, T., Xie, X., Jiang, W., Li, J., Tian, B., and Su, C. (2019). Oxygen-functionalized Ultrathin Ti_3C_2 T_x MXene for enhanced electrocatalytic hydrogen evolution. ChemSusChem *12*, 1368–1373. https://doi.org/10.1002/cssc.201803032.

5. Bat-Erdene, M., Batmunkh, M., Sainbileg, B., Hayashi, M., Bati, A.S.R., Qin, J., Zhao, H., Zhong, Y.L., and Shapter, J.G. (2021). Highly Dispersed Ru nanoparticles on boron-doped Ti3C2Tx (MXene) nanosheets for synergistic Enhancement of electrocatalytic hydrogen evolution. Small *17*, e2102218. https://doi.org/10.1002/smll.202102218.

6. Dhiman, M., and Polshettiwar, V. (2018). Supported Single Atom and Pseudo-single Atom of Metals as Sustainable Heterogeneous Nanocatalysts. *ChemCatChem*, *7* (Wiley Blackwell March), pp. 881–906. https://doi.org/10.1002/cctc.201701431.

7. Liu, H., Hu, Z., Liu, Q., Sun, P., Wang, Y., Chou, S., Hu, Z., and Zhang, Z. (2020). Single-atom Ru anchored in nitrogen-doped MXene (Ti3C2T: X) as an efficient catalyst for the hydrogen evolution reaction at all PH Values. J. Mater. Chem. A Mater. *8*, 24710–24717. https://doi.org/10.1039/d0ta09538a.

8. Peng, Y., Zhang, Y., Guo, A., Mao, M., Wang, Y., Long, Y., and Fan, G. (2022). Universal low-Temperature Oxidative Thermal Redispersion strategy for green and sustainable Fabrication of Oxygen-Rich carbons anchored metal nanoparticles for hydrogen evolution reactions. Chem. Eng. J. *433*, 133648. https://doi.org/10.1016/j.cej.2021.133648.

9. Ramalingam, V., Varadhan, P., Fu, H.C., Kim, H., Zhang, D., Chen, S., Song, L., Ma, D., Wang, Y., Alshareef, H.N., and He, J.H. (2019). Heteroatom-mediated interactions between ruthenium Single atoms and an MXene support for efficient hydrogen evolution. Adv. Mater. *31*, e1903841. https://doi.org/10.1002/adma.201903841.

10. Uwadiunor, E., Kotasthane, V., Yesudoss, D.K., Nguyen, H., Pranada, E., Obodo, K., Radovic, M., and Djire, A. (2023). Pt-Like catalytic activity from an Atomistically Engineered carbonitride MXene for sustainable hydrogen production. Chem Catal.100634 https://doi.org/10.1016/J.CHECAT.2023.100634.