GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL

4-10 July 2021 Venezia, Italy

Hierarchical Metal–Polymer Hybrids for Enhanced CO_2 Electroreduction

Shuaiqiang Jia, Qinggong Zhu,* Mengen Chu, Shitao Han, Ruting Feng, Jianxin Zhai, Wei Xia, Mingyuan He, Haihong Wu,* and Buxing Han*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University

Introduction

Electrochemical conversion of CO_2 into value-added products has become one of the most promising routes to utilize abundant CO_2 feedstocks under ambient conditions. While metal-based heterogeneous catalysts commonly exhibit high activity for CO_2 reduction reaction (CO_2RR), achieving high activity, selectivity and stability simultaneously remains a challenge. Hybrid has emerged as an effective method for solving the above problem. Among them, metal-polymer hybrids offer the advantage of controlling the microenvironment of the active site motifs. So far, the metal/polymer hybrids have been successfully applied as electrocatalysts for CO_2RR by a straightforward modification method. However, effects of the microenvironment on the catalytic properties are still inconclusive. Based on these considerations, some questions arise: 1) How to manipulate the metal/polymer structure to create a desirable reaction microenvironment? 2) How they critically influence the catalytic performance of CO_2RR? Study on these issues are helpful to design the efficient catalysts. But conventional synthetic strategies have limitation due to their difficulty in delicate control of the structure.

Herein, we report an approach to design of metal/polymer hybrids, which allows control of effective structure capable of hosting active sites stably for CO_2RR. A series of three-dimensional (3D) hierarchically structured metal/polymer hybrids ((Cu, Pd, Zn, Sn)/polymer) were synthesized.

Methods

The metal/polymer hybrid with 3D hierarchical structure was synthesized by coupling a continuous electrodeposition process as shown in route I The polymer layer was first formed on the carbon paper (CP) network by in situ electro-polymerization. Subsequently, 3D metal layer is decorated on the polymer-CP by electrodeposition to obtain M/polymer-CP (I). Conventional strategies, including drop-coating of metal NPs on the polymer/CP obtained by electrodeposition (M/polymer-CP (II)), drop-coating of the solvothermal synthesized metal/polymer hybrid on CP (M/polymer-CP (III)), and direct electrodeposition of metal NPs on CP by electrodeposition (M-CP (IV)) were also carried out for comparison By route I (this work), catalysts with different metals (Cu, Pd, Zn, Sn) and conducting polymers (PANI), polypyrrole (PPy), polythiophene (PTh), and their co-polymers) were prepared .

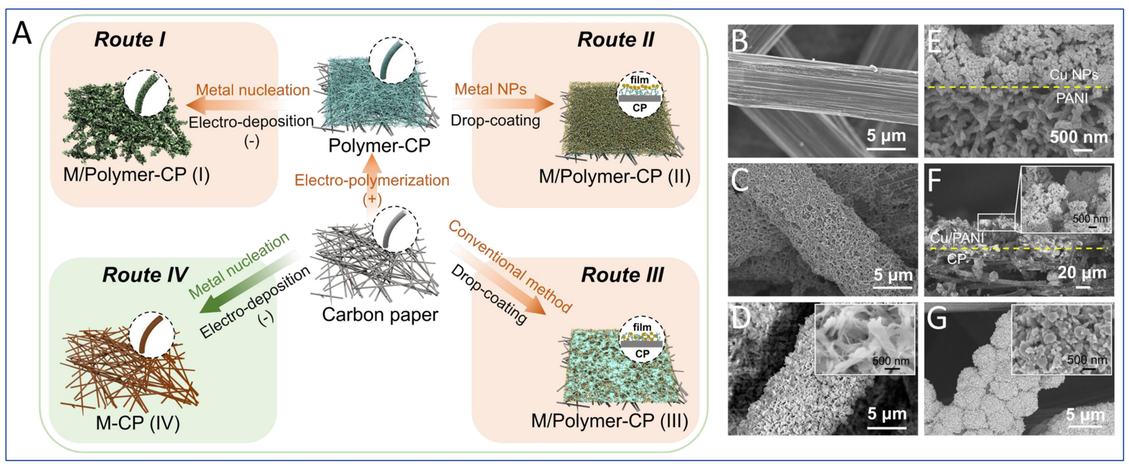

Figure #1

Results

A C_2H_4 Faradaic efficiency of 59.4% with a current density of 30.2 mA cm^{-2} could be achieved using Cu/PANI-CP electrode in an H-type cell, and the electrode was very stable.

Considering all of observations above, we conclude that the 3D hierarchical structure obtained by in situ synthetic strategy is critical to enhance activity, selectivity and stability. These are further discussed below:

1. The in situ synthetic strategy creates a favorable microenvironment to promote activity.
2. The 3D hierarchical structure enhances selectivity.
3. High dispersion of metal nanosheets improve stability.

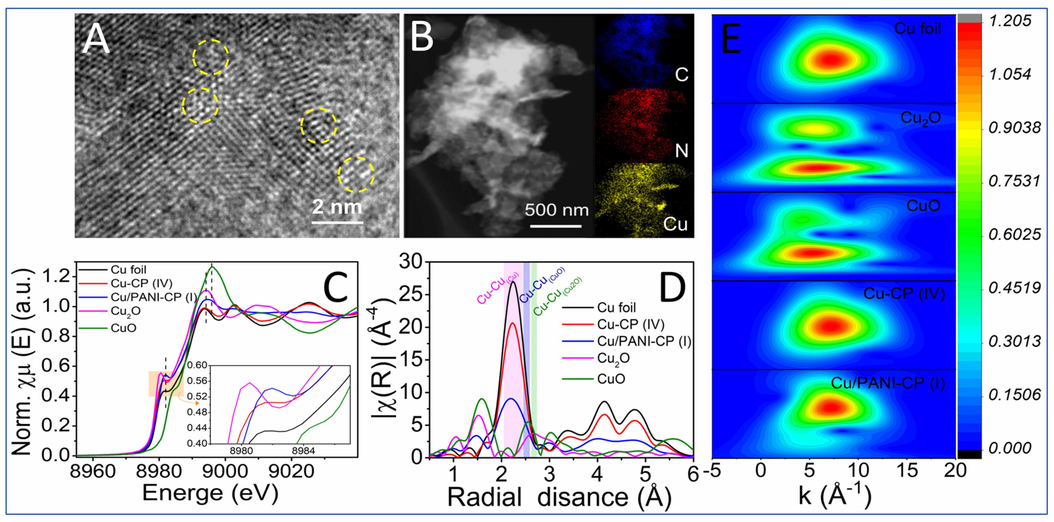

Figure #2

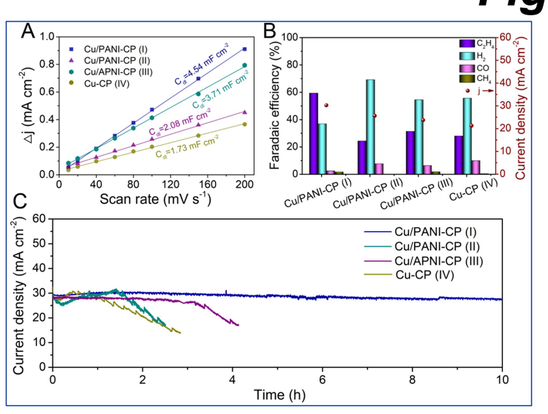

Figure #3

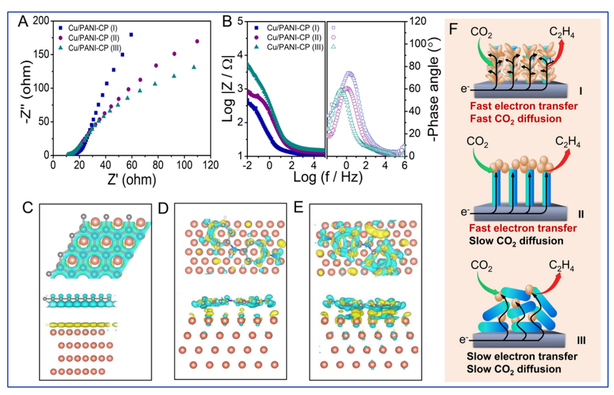

Figure #4

Conclusions

In summary, we have presented an approach to fabricate 3D hierarchical M/polymer-CP electrodes for CO_2 electroreduction via in situ electrodeposition. The enhancement of selectivity is also due to the longer staying time of intermediates in the catalyst layer, providing more opportunity for their coupling to form a desired product. Moreover, the 3D hierarchical structure results in high dispersion of the metals, which prevents agglomeration of metals and thus improves stability. We believe that the in situ synthetic strategy has wide application in design and fabrication of advanced electrocatalysts for CO_2 electroreduction.

References

[1] a) S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Norskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.* **2019**, *119*, 7610-7672; b) Z. Sun, T. Ma, H. Tao, Q. Fan, B. Han, *Chem* **2017**, *3*, 560-587.

[2] a) D. H. Nam, P. De Luna, A. Rosas-Hernandez, A. Thevenon, F. Li, T. Agapie, J. C. Peters, O. Shekhah, M. Eddaoudi, E. H. Sargent, *Nat. Mater.* **2020**, *19*, 266-276; b) Z. Weng, J. Jiang, Y. Wu, Z. Wu, X. Guo, K. L. Materna, W. Liu, V. S. Batista, G. W. Brudvig, H. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 8076-8079.

[3] a) X. Wei, Z. Yin, K. Lyu, Z. Li, J. Gong, G. Wang, L. Xiao, J. Lu, L. Zhuang, *ACS Catal.* **2020**, *10*, 4103-4111; b) Y. Yang, Y. Zhang, J. Hu, L. Wan, *Acta Phys. -Chim. Sin.* **2020**, *36*, 1906085.