nature communications

Article

https://doi.org/10.1038/s41467-024-46098-x

Single-atom tailored atomically-precise nanoclusters for enhanced electrochemical reduction of CO_2-to-CO activity

Received: 5 September 2023

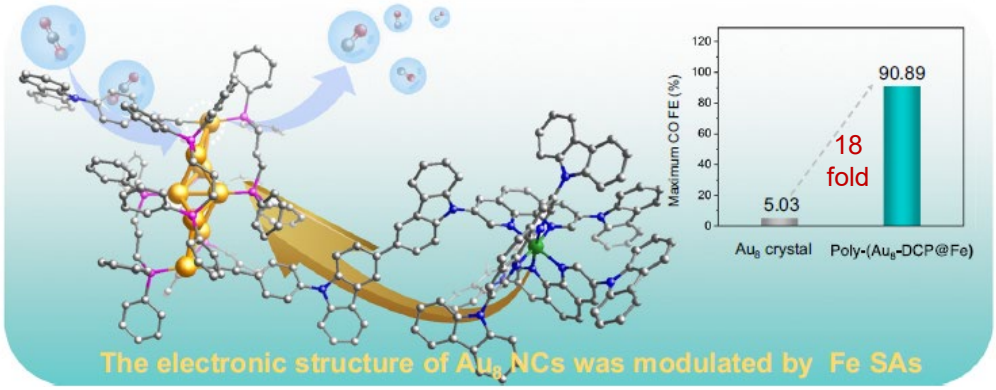
Accepted: 13 February 2024

Published online: 28 February 2024

Yi-Man Wang[1], Fang-Qin Yan[1], Qian-You Wang[1], Chen-Xia Du[1], Li-Ya Wang[2], Bo Li[2], Shan Wang[1] ✉ & Shuang-Quan Zang[1] ✉

Swetashree Acharya

17.08.2024



[1]Henan Key Laboratory of Crystalline Molecular Functional Materials, College of Chemistry, Zhengzhou University, Zhengzhou 450001, China. [2]College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China. ✉e-mail: shanwang@zzu.edu.cn; zangsqzg@zzu.edu.cn

Background Studies

Angewandte International Edition Chemie
GDCh A Journal of the German Chemical Society

Communication

A Tandem Strategy for Enhancing Electrochemical CO_2 Reduction Activity of Single-Atom Cu-S_1N_3 Catalysts via Integration with Cu Nanoclusters

Datong Chen, Dr. Lu-Hua Zhang, Dr. Jian Du, Prof. Honghai Wang, Jiangyi Guo, Jiayu Zhan, Prof. Fei Li, Dr. Fengshou Yu

First published: 08 September 2021 | https://doi.org/10.1002/anie.202109579 | Citations: 99

Usually involves pyrolysis treatment

Resulting catalyst with vague structure makes it difficult to decipher structure–activity relationships

Angewandte International Edition Chemie
GDCh A Journal of the German Chemical Society
Angewandte Chemie International Edition homepage

Research Article | Full Access

Modulating Electronic Structures of Iron Clusters through Orbital Rehybridization by Adjacent Single Copper Sites for Efficient Oxygen Reduction

Chunhong Qi, Haoyu Yang, Ziqi Sun, Haifeng Wang, Na Xu, Guihua Zhu, Lianjun Wang, Wan Jiang, Xiqian Yu, Xiaopeng Li, Qi Xiao, Pengpeng Qiu, Wei Luo

First published: 24 July 2023 | https://doi.org/10.1002/anie.202308344 | Citations: 12

Motivation

- Despite their structural appeal, generally poor stability and catalytic properties of NCs put them out of reach of practical applications.
- The goal of achieving a metal NCs based catalyst with high activity and stability raises the necessity for the development of new tailoring approach.

Why this paper?

- This work contribute to explore the intrinsic activity and stability improvement of metal clusters.
- Here, uniformly dispersed metal NCs modified with SA site catalysts were achieved through an effective co-eletropolymerization strategy.

Introduction

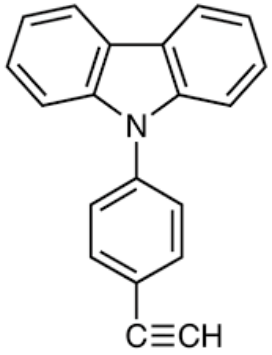
- Extensive research efforts have been devoted to improving the catalytic properties of metal NCs by tailoring their compositions and structures, such as heterometallic doping, ligand engineering, and size regulating.

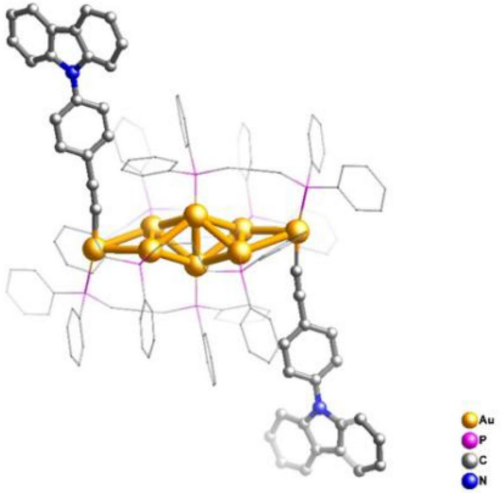
- This strategy fixing nanoclusters and single-atoms on cross-linked polymer networks efficiently deduce the performance deactivation caused by agglomeration during the catalytic process.

- Considering that gold-based nanomaterials are intrinsically active for catalyzing CO_2 reduction reaction (CO_2RR), Au_8 NC $[Au_8(dppp)_4(CzPA)_2]^{2+}$ capped by bidentate pisphosphine (dppp = 1,3-bis(diphenylphosphino) propane) and alkynyl carbazole ligands (HCzPA, 9-(4-ethynylphenyl)carbazole) was chosen as the model NC.

- Fully pre-disperse the well-defined metal NCs and SAs by this strategy, making them evenly distributed in the resulting skeleton, provides ideal platforms to understand the critical roles of NCs and SAs in catalytic processes.

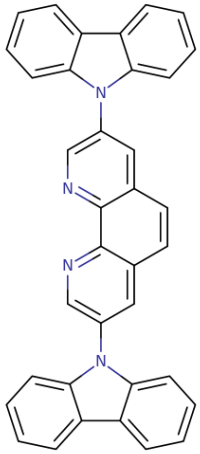
Synthesis

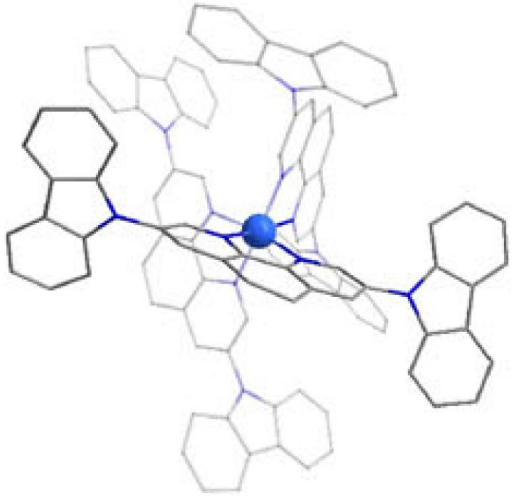




9-(4-ethynylphenyl)carbazole (HCzPA)

$[Au_8(dppp)_4(CzPA)_2]^{2+}$

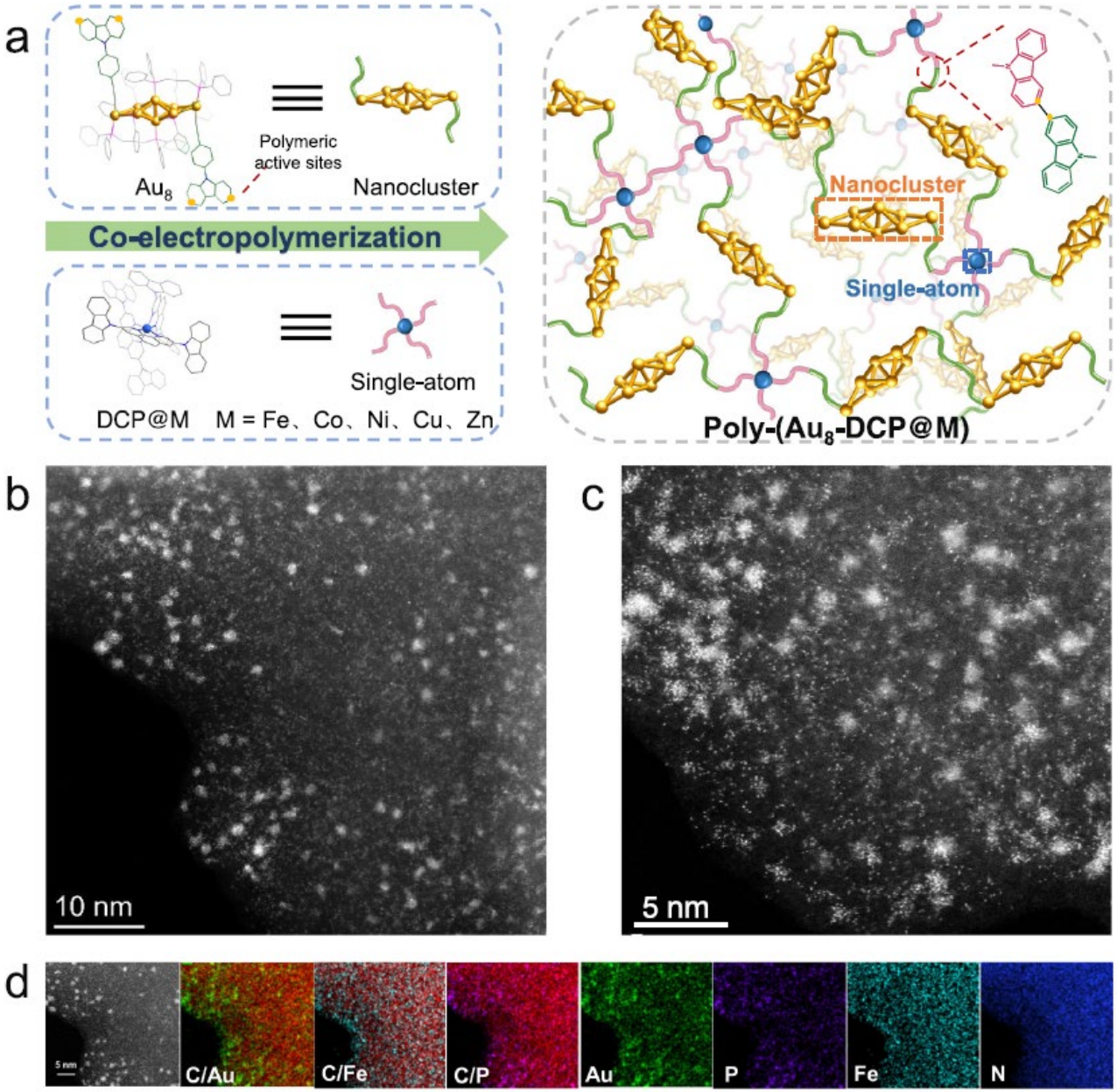




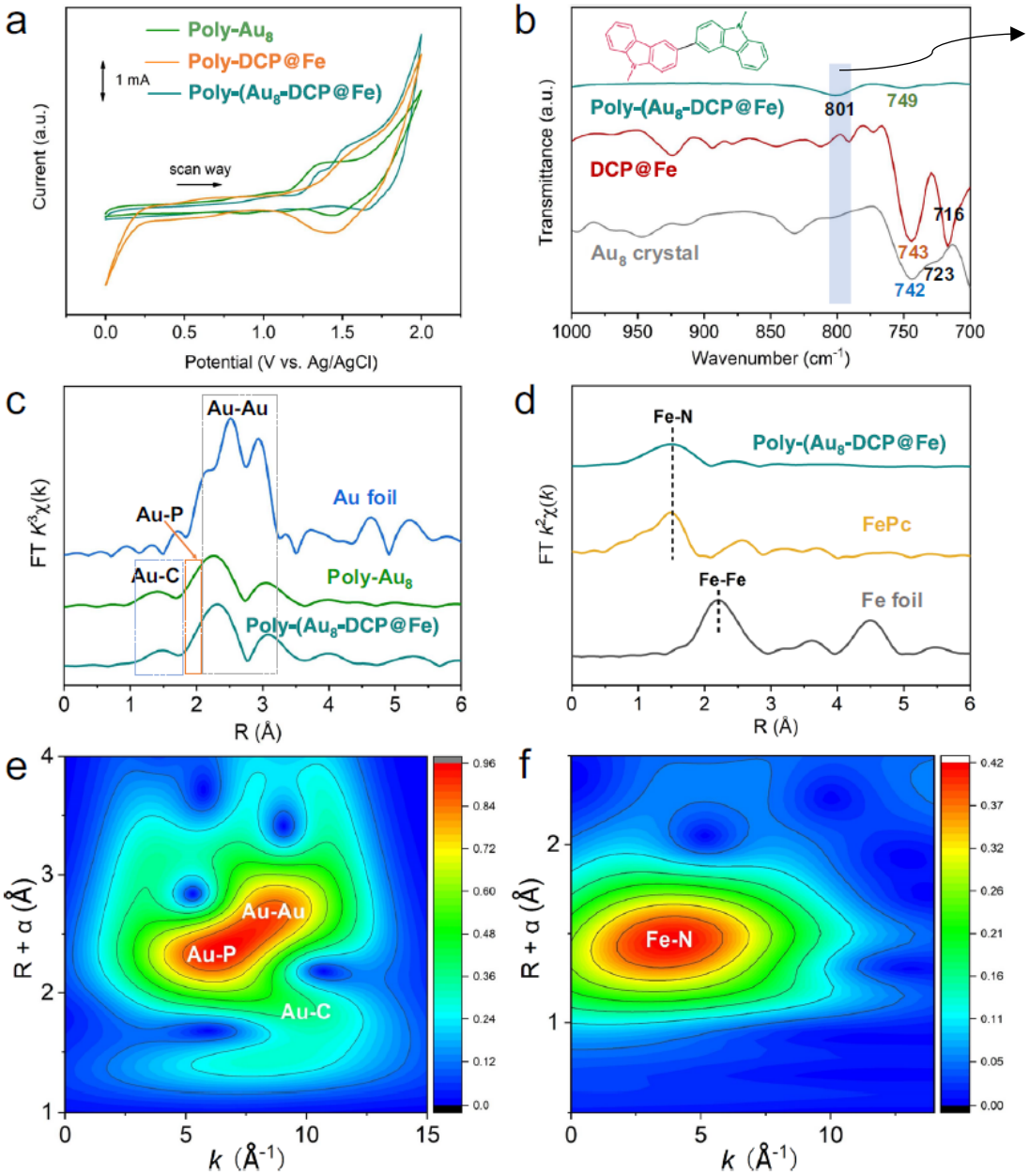
3,8-di(9H-carbazol-9-yl)-1,10-phenanthroline (DCP)

DCP@M (M=Fe, Co, Ni, Cu, Zn)

Synthesis procedure and morphology characterizations of the catalysts

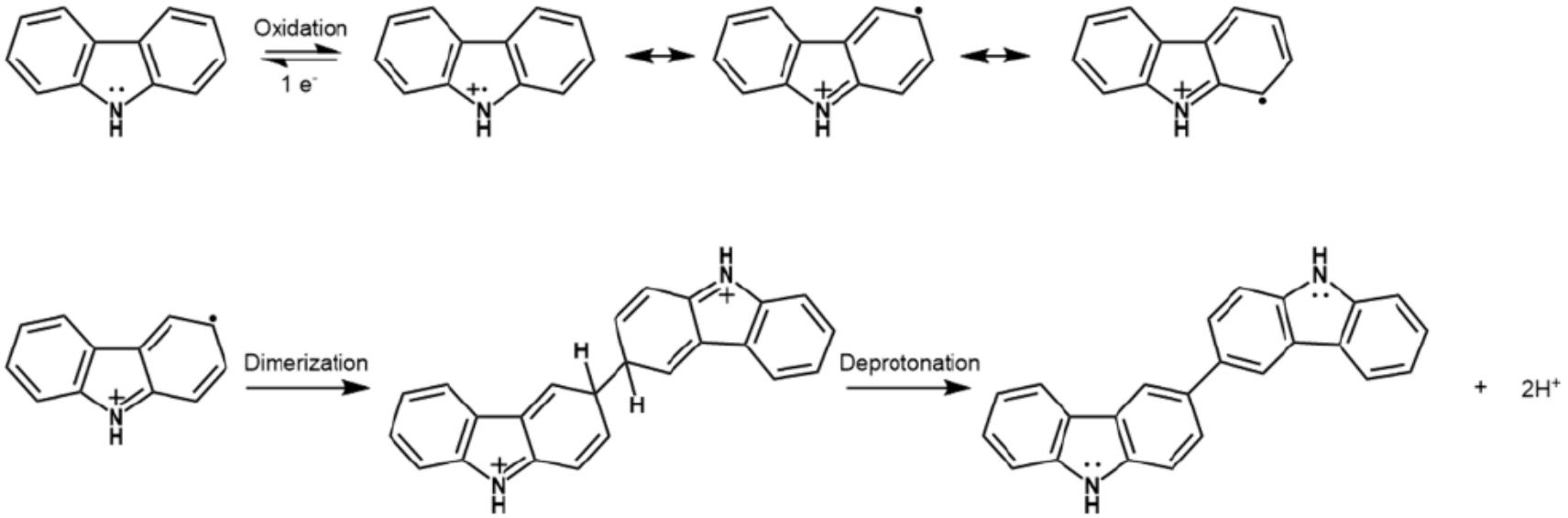


Structural analysis of Poly-(Au8-DCP@Fe)



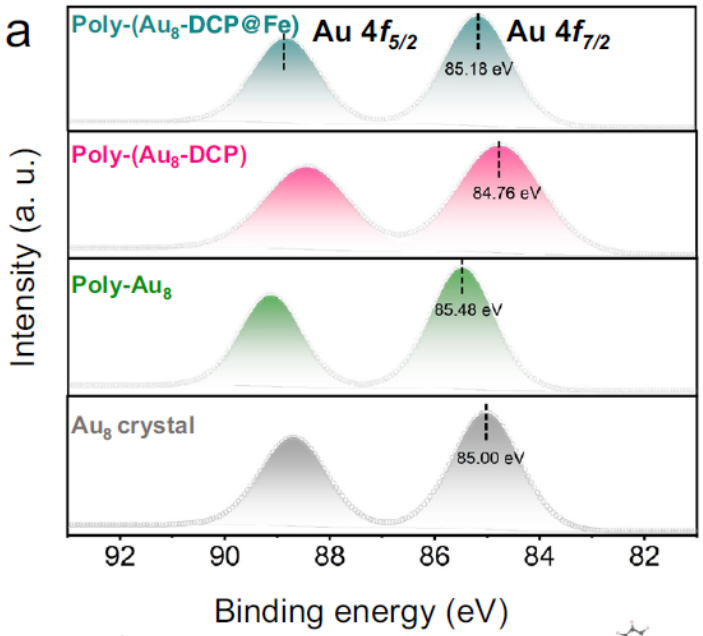
Vibrational band of C-H bond

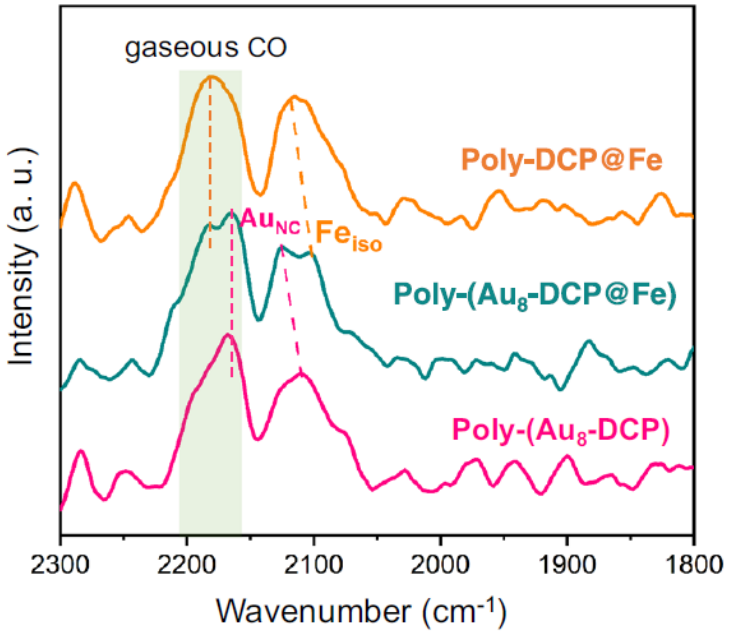
Electropolymerization mechanism of carbazole

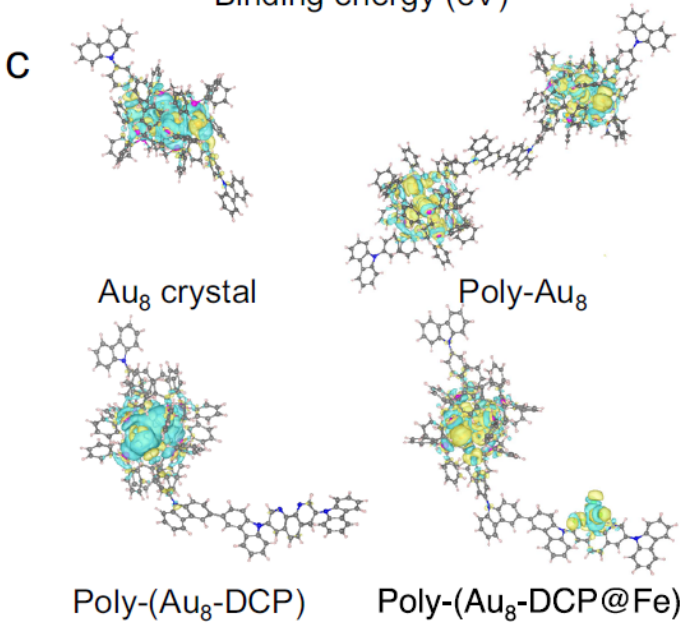


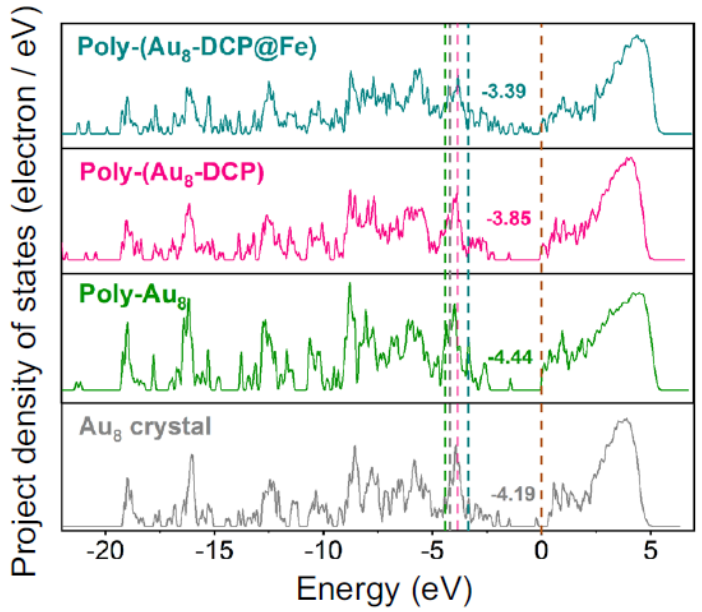
Study on electronic structure of Poly-(Au_8-DCP@Fe)

Indicates increase in $Au^{\delta+}$ species.

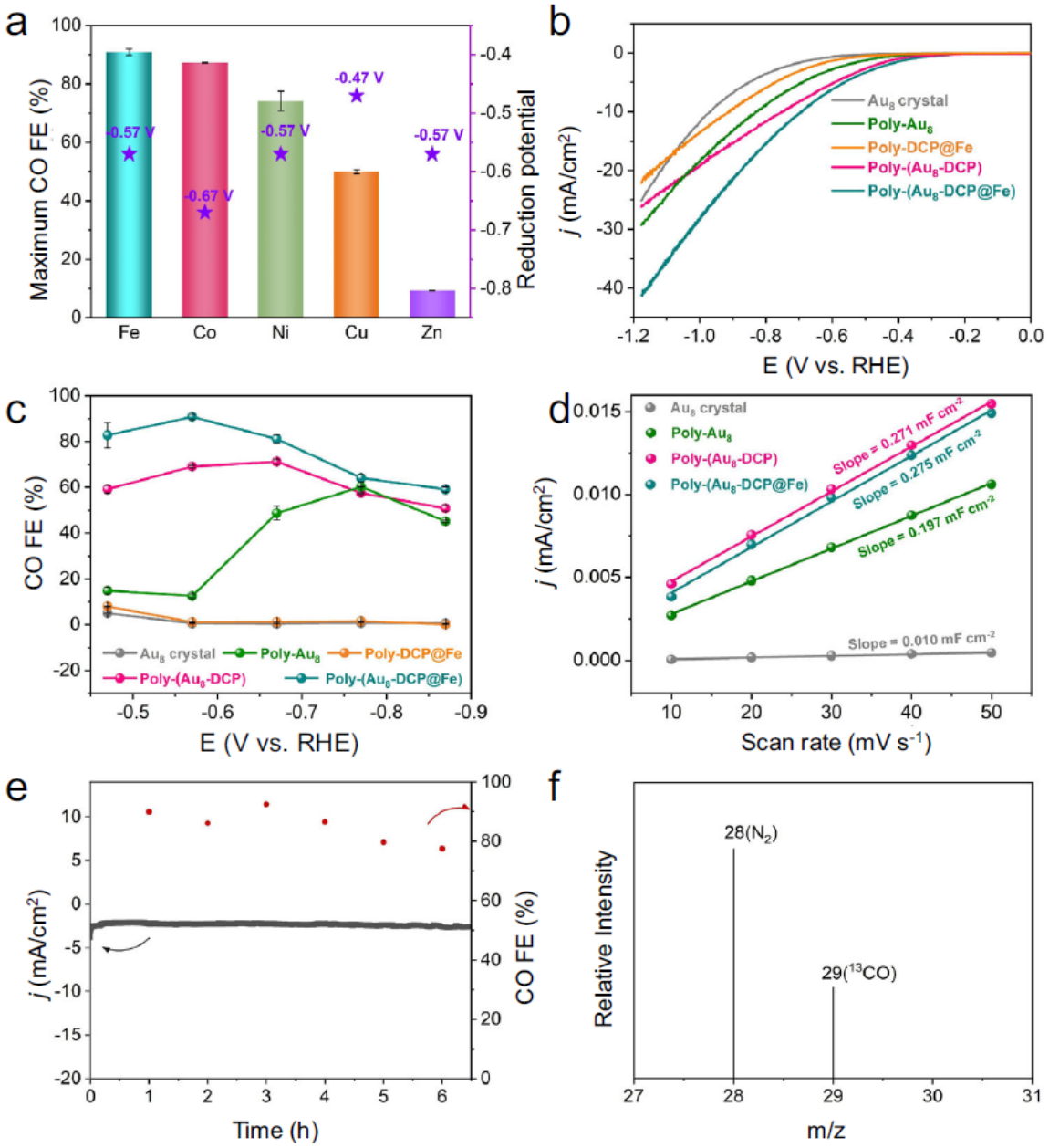






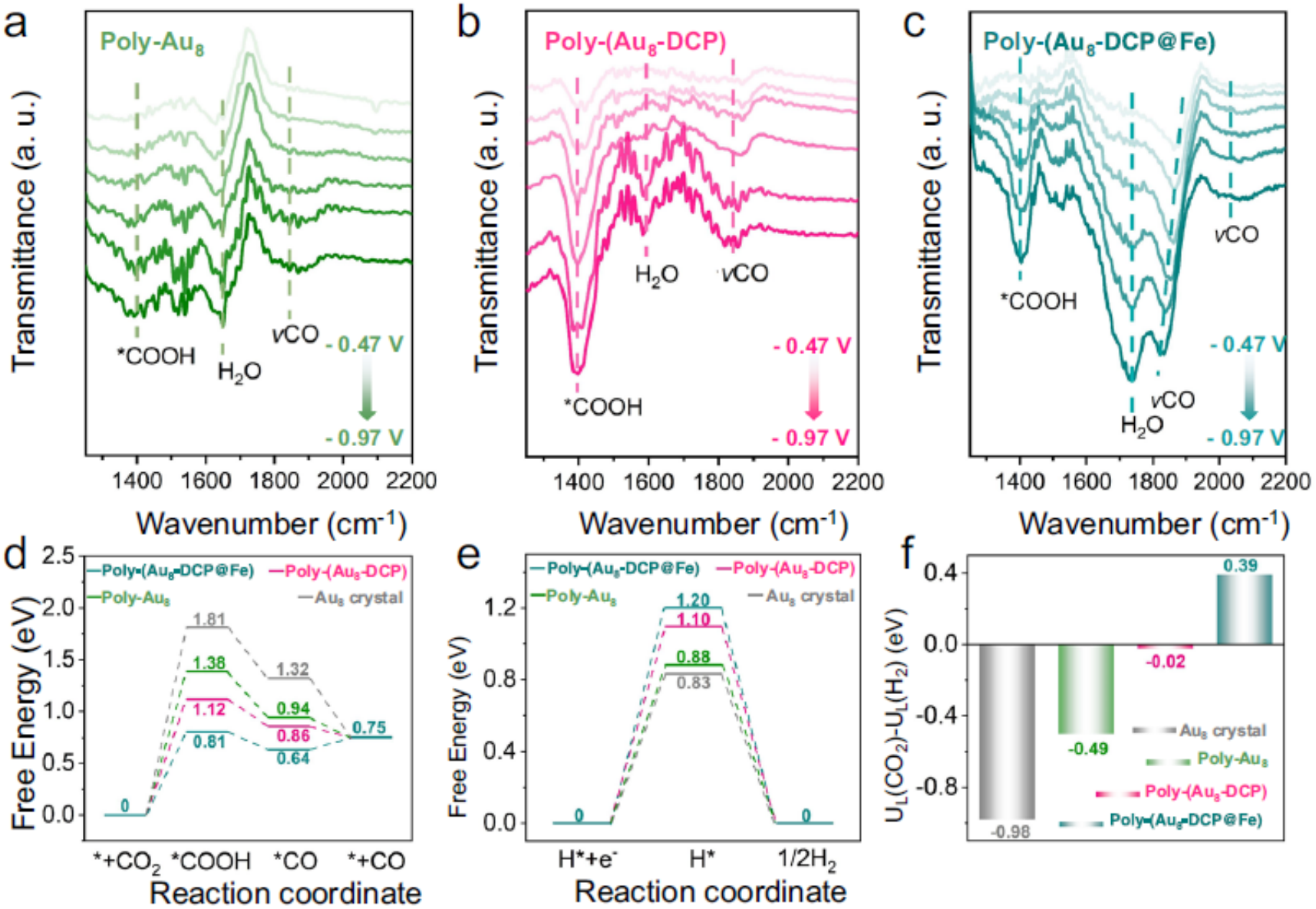


Electrocatalytic CO_2 reduction performance



Slope = electrochemical double layer capacitance

In situ ATR-FTIR and theoretical studies



Conclusion

- They have successfully constructed a highly homogeneous NC-SA hybrid catalyst Poly-(Au_8-DCP@Fe) by facile coeletropolymerization strategy.

- The obtained Poly-(Au_8-DCP@Fe) featured a considerably enhanced catalytic performance toward CO_2RR—a 90.89% CO FE at −0.57 V, than that of SA or metal NC components.

- The detailed analysis revealed that the high catalytic activity of Poly-(Au_8-DCP@Fe) derive from the effective regulation of the electronic structure of the Au_8 NCs by the Fe SAs, in which the Fe SA showed a positive modulation on the charge density and projected density of states of the metal cluster sites.

- This work creatively presented a new strategy to regulate the inherent catalytic activity of metal NCs via the introduction of SAs.