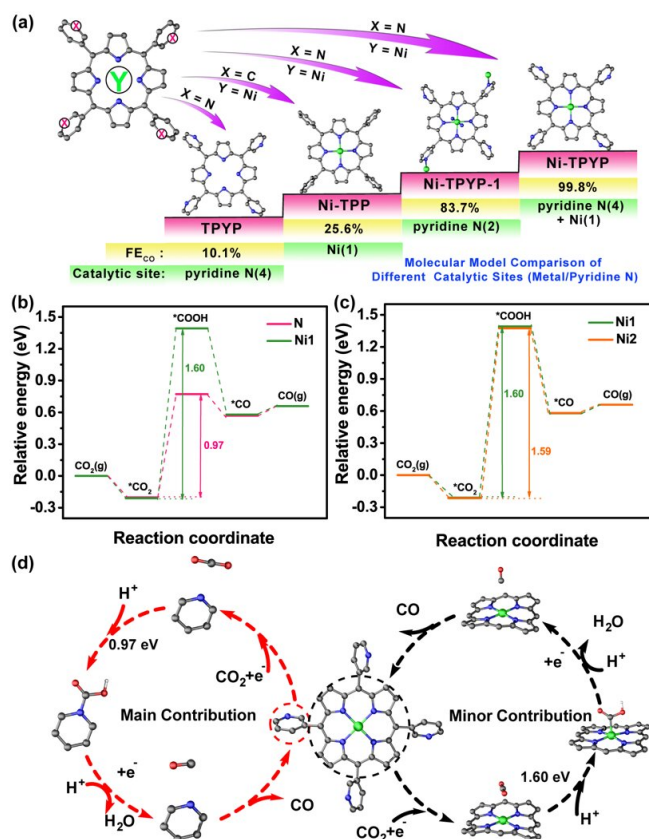


Stable supramolecular structure system to identify activity origin of carbon dioxide electroreduction

28 September 2020



(a) Comparison of different molecular structures and catalytic sites (Ni-TPYP, Ni-TPYP-1, Ni-TPP and TPYP), (b, c) Calculated free energy profile for CO₂ reduction reaction toward the production of CO, (d) Simulated CO₂-to-CO conversion reactive pathway over Ni-TPYP molecule. Credit: Authors

N-doped or N-heterocyclic nanostructured electrocatalysts for electrocatalytic CO₂ reduction reaction have made important progress in product selectivity. For further development, it is important to identify the exact activity origin of these electrocatalysts. Crystal electrocatalysts with accurate structures can provide a visual research

platform for identifying catalytic active sites and studying reaction mechanism. The catalytic activity of pyridine N for CO₂ electroreduction was first determined structurally by crystal supramolecular coordination compound model system.

CO₂ electroreduction reaction driven by renewable electricity is an effective way to reduce the concentration of CO₂ in the atmosphere and alleviate [environmental problems](#) such as global warming. It can convert CO₂ into valuable products (such as CO, HCOOH, CH₄) to realize an effective carbon cycle. At present, the reported highly efficient electrocatalysts for electrocatalytic CO₂ reduction reaction (CO₂RR) are mainly concentrated on nanomaterials. Among them, N-doped or N-heterocyclic nanostructured electrocatalysts have made important progress in reduction product conversion and Faraday efficiency. However, due to the lack of accurate and clear structural information and other influencing factors (including defects and impurities), it is still difficult to determine the [activity](#) of N sites in these electrocatalysts.

In this case, crystal electrocatalysts with clear crystal structure have great advantages in solving the above problems, because their accurate structure information can provide a visual research platform for identifying catalytic active sites and studying [reaction mechanism](#). Metalloporphyrin complexes applied in CO₂RR have many advantages. Among them, the rigid ring with conjugated π - electron system of metalloporphyrin is favorable to rapid electron migration. More importantly, their clear molecular structure information and structural tunability are very helpful for studying reaction mechanisms and rationally optimizing catalytic performance.

Based on this, establishing a reasonable crystal

model system to accurately identify the activity of catalytic sites in electrocatalysis is very important for the development of electrocatalytic CO₂RR.

In a new research paper published in *National Science Review (NSR)*, the research group of professor Ya-Qian Lan of Nanjing Normal University, for the first time established a crystal supramolecular coordination compound model system (including Ni-TPYP, Ni-TPYP-1 and Ni-TPP, as shown in Figure 1) to identify structurally the catalytic activity of pyridine N for electrocatalytic CO₂RR. This work is of great significance for understanding the catalytic activity and reaction mechanism of N-doped or N-heterocyclic nanostructured electrocatalysts in electrocatalytic CO₂RR.

Experimental and theoretical calculations show that the rate determining step (RDS) of electrocatalytic CO₂RR in this system is the formation of COOH. In this step, the energy required for the Ni active site (denoted as Ni1) in Ni-TPYP and the Ni active site (denoted as Ni2) in Ni-TPP are almost the same (1.60 eV and 1.59 eV) and both are higher than that of active pyridine N (denoted as N, 0.97 eV) in Ni-TPYP, indicating that N site has higher CO₂ electroreduction activity than Ni2 and Ni1 sites, that is, active pyridine N is a more suitable catalytic active [site](#).

More information: Sheng-Nan Sun et al, Identification of the activity source of CO₂ electroreduction by strategic catalytic site distribution in stable supramolecular structure system, *National Science Review* (2020). DOI: [10.1093/nsr/nwaa195](https://doi.org/10.1093/nsr/nwaa195)

Provided by Science China Press
APA citation: Stable supramolecular structure system to identify activity origin of carbon dioxide electroreduction (2020, September 28) retrieved 24 November 2020 from <https://phys.org/news/2020-09-stable-supramolecular-carbon-dioxide-electroreduction.html>

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