

Advancing redox-chemistry-based energy science is one of the most urgent challenges in the 21st century. The milestone developments in this field have often been made by understanding basic problems on reaction mechanisms. Especially, the structure-property correlations on electrode materials are crucially important in both electrochemical energy storage and electrocatalysis. Therefore, solving fundamental questions can provide striking impacts to present key energy technologies.

In order to contribute to this grand challenge, I am focusing on unveiling microscopic energy transformation mechanisms in electrochemistry by using a wide spectrum of two-dimensional (2D) conjugated frameworks as model electrodes. Here, I show two main achievements from my recent works.

### **(1) Tuning Energy Storage Mechanism with Designer Frameworks**

Density of states (DOS) is well-known as a key quantity to control electrochemical properties: DOS is directly linked to the theoretical electron transfer number of an electrode material at a specific potential. However, it is still difficult to picture the principle ruling microscopic electronic interactions in electrode materials, and therefore the principle controls DOS. Furthermore, the one-electron cationic redox is usually the main reason for the limitation of specific energy density. In order to solve these issues, I used two-dimensional 2D conjugated frameworks (2DCFs), such as covalent organic frameworks (COFs) and coordination frameworks, as well-defined model electrode systems to uncover fundamental effects of electronic structure for tuning microscopic energy storage mechanism.

I designed electrode materials based on COFs which have the DOS, contributing to multi redox-reactions, and showed that we can obtain multi-electron transfer energy storage mechanism (*Angew. Chem. Int. Ed.* **2012**; *Nat. Commun.* **2013**). Furthermore, based on these works, I investigated a series of conductive coordination frameworks as model intercalation electrode materials (*Angew. Chem. Int. Ed.* **2018**). As the result, we found out that we can improve the electron-transfer number with fine-tuned hybridizations of the metal cation's 3d-orbital and the ligand's p-orbital, which leads to access a tunable cationic/anionic mixing redox mechanism.

### **(2) Tuning Energy Conversion Process with 2D Conjugated Frameworks**

Surface states of electrocatalysts can give huge impact to efficiency and selectivity of energy conversion processes (*J. Am. Chem. Soc.* **2015**, *Phys. Rev. Lett.* **2018**). I introduced a new approach to tune the processes by using heterojunction-based electrocatalysts with 2D conjugated frameworks (2DCFs), which can provide a mesoscopic flexibility being often a key for many efficient reactions (*ACS Nano* **2017**). On the metal surfaces, the 2DCFs can form large junction areas between the edges of the pores and the metal support, which can play a role in the catalytically active sites. In addition to this, in the case of the heterojunction based on 2DCFs, there are spaces between corrugated frameworks and metals, which can be tiny containers where catalytic reactions can take place (*Acc. Chem. Res.* **2015**). For the proof of concept, we used carbon- nitrogen-based frameworks and gold as a model system, and oxygen reduction reaction and hydrogen evolution reaction as model reactions. The experiment/theory combined work successfully showed that heterojunction with 2DCFs can provide complementary adsorption sites for reactants at the 2DCF/metal interface therefore can lead to more efficient reaction pathways.