

# In-situ X-ray Absorption Spectroscopy Investigation on Au Nanoparticle Decorated Trimetallic Metal–Organic Frameworks as High Efficient Oxygen Evolution Reaction Electrocatalysts

Chih-Chieh Cheng<sup>1</sup>, Po-Yin Cheng<sup>1</sup>, Chun-Lung Huang<sup>1</sup>, Duraisamy Senthil Raja<sup>1</sup>, Yen-Ju Wu<sup>1</sup>, and Shih-Yuan Lu<sup>1\*</sup>

<sup>1</sup> Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

\*Email: sylu@mx.nthu.edu.tw (S.-Y. Lu)

## Abstract

Hydrogen production through electrochemical water splitting is a promising approach for renewable energy storage. Nevertheless, the involved oxygen evolution reaction (OER) constrains the overall electrochemical water splitting efficiency. Therefore, developing high efficiency and cost-effective electrocatalysts as well as investigating the mechanism for the OER attract great research attention. Engineering electronic states through decoration of functional entities is an effective way to advance catalyst design. In this work, Au nanocrystal decorated Fe, Co and Ni based trimetallic MOFs, grown in-situ on nickel plates (termed Au/(FCN)MOF/NP), were developed as high efficiency OER electrocatalysts, achieving significantly improved OER performances over the (FCN)MOF/NP electrode. It lowered  $\eta_{10}$  and  $\eta_{500}$  from 241 and 340 mV to 216 and 290 mV, respectively, Tafel slope from 42.1 to 31.4 mV dec<sup>-1</sup>, and current density decay from 6 to 5% after 50 hour operations at an initial current density of 160 mA cm<sup>-2</sup>. The positive synergistic effects between trimetallic MOF and Au nanocrystals can be attributed to the elevated average oxidation states of Fe, Co and Ni, caused by the high electronegativity of Au nanoparticles and evidenced with high resolution X-ray photoelectron spectroscopy (HR-XPS) and in-situ Raman spectroscopy, which lead to formation of active species of high oxidative potentials and thus high catalytic efficiency toward the OER. Furthermore, potential-resolved in-situ X-ray absorption spectroscopy (in-situ XAS) measurements were conducted to further study the OER mechanism of Au/(FCN)MOF/NP. The main active metal centers were identified with the in-situ XAS study to be Ni and Co, exhibiting increasing extent of coordination with OH<sup>-</sup> at increasing applied potentials and thus formation of active intermediates to trigger the OER. Of particular interest is the potential-dependent transformation of  $\alpha$ -Ni(OH)<sub>2</sub> phase to more OER-active  $\gamma$ -NiOOH (Ni<sup>3+/4+</sup>) phase at increasing applied potentials. Fe, on the other hand, being relatively inert toward the OER, exhibiting no appreciable changes in coordination environment at increasing applied potentials, plays a supporting role to help Ni acquire high valence states to realize enhanced OER activities.

**Keywords** - oxygen evolution reaction; gold nanocrystal; engineering electronic state, in-situ Raman spectroscopy; in-situ X-ray absorption spectroscopy