Atomically Dispersed Photoelectrocatalysts

Chunhua Cui*, Yanbo Li

Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China.

**Corresponding author: chunhua.cui@uestc.edu.cn*

Abstract: Atomically dispersed catalysts can maximize atom efficiency and minimize cost. We have addressed the stability and loading issue by designing a robust and atomically dispersed catalyst that was in-situ immobilized on semiconductor under turnover. By designing Ir and Ni-based molecular models, we present how soluble active species could be able to be immobilized on the semiconductor surface and catalyze the water oxidation. We thus bridged the communication between the soluble catalyst species and the semiconductor surfaces and exhibited unprecedented performance stability.

Keywords: single atom, water splitting, in-situ immobilization.

1. Introduction

Owing to the slow kinetic process, the photoelectrochemical (PEC) water oxidation is the most difficult part in artificial photosynthesis because the oxygen evolution reaction (OER) with four-electron process per molecule of oxygen exhibits extremely small exchange current density, compared to the hydrogen evolution reaction with two-electron process per molecule of hydrogen.[1] Except for the development of high performance semiconductors,[2] a prerequisite for these technologies is the development of highly efficient and stable catalysts for PEC devices.

2. Experimental

We have addressed the stability issue by designing an atomically dispersed hybrid Ni-Ir catalyst that was prepared on hematite support by electrostatic adsorption of soluble monomeric $[Ir(OH)_6]^{2-}$ coupled to pre-loaded and positively charged MO_x sites (M=Fe, Cu, Co, Ni, and Ti) under turnover as shown in Fig.1.[3]

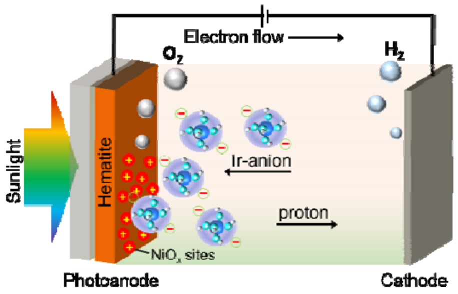

Fig. 1 Schematic illustration of the molecular loading process.

3. Results and discussion

As an ideal molecular model, we present a close relationship between the hole accumulation capacity of MO_x and the enhanced activity of $[Ir(OH)_6]^{2-}$ by screening the MO_x sites. We reveal that NiO_x has the highest capacity of hole accumulation and the instant formation of "Fe/Ni-O-Ir" bonds during OER, allowing the accumulated holes subsequently transfer to Ir sites. We thus bridged the communication between the soluble catalyst species and the semiconductor surfaces. More importantly, this hybrid catalyst exhibited unprecedented performance stability in alkaline electrolyte for more than 80 hours of operation.

4. Conclusions

In summary, this is a totally inorganic hybrid catalyst that combines the advantages of soluble molecular catalysts with fully exposed active sites and the benefits of solid-state materials with unique physicochemical properties, bridging the gap between heterogeneous and homogeneous catalysts.

References

1. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
2. T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520-7535.
3. C. Cui, M. Heggen, W.-D. Zabka, W. Cui, J. Osterwalder, B. Probst and R. Alberto, *Nature Comm*, 2017, **8**, 1341.