Thin layer Ni-MOF as efficient photosensitizer for TiO₂ nanorods array and application to photoelectrochemical water splitting

Sheng-Mu You^{1,2}, Waleed M.A. El Rouby^{1,3}, Ruey-An Doong^{2,4*}, Pierre Millet^{1*}

1. Paris-Sud University, ICMO-Eriée, UMR CNRS 8182, 91405 Orsay, France.

2. National Chiao Tung University, Institute of Environmental Engineering, 30010, Taiwan.

3. Materials Science and Nanotechnology Department, PSAS, Beni-Suef University, 62511 Beni-Suef, Egypt.

4. National Tsing Hua University, Institute of Analytical and Environmental Science, 30013, Taiwan.

國立交通大學
National Chiao Tung University

Abstract

Photoelectrochemical (PEC) water splitting has been widely regarded as one of the most promising routes for hydrogen evolution in the recent years since the TiO₂ base materials were used. The surface modification is necessarily required to develop a variety of hybrid titanium dioxide (TiO₂) nanostructures for the application of water splitting under solar light. In this work, we successfully decorated thin layer structure of Ni-MOF on the TiO₂ nanorods (TDNRs) using a layer-by-layer process. The morphology analysis shows the oriented TNR were grown with Ni-MOF nanoparticles to become the foam-like nanostructures. The unique architecture of Ni-MOF/TDNR photoanode shows enhanced activity with a photocurrent of 0.46 mA cm⁻² under UV + Visible light and 42.4 μA cm⁻² under visible light (>420 nm) which are far more than the bare TNRs (>20 times). However, the loading concentration of Ni-MOF highly impacts the resistance, electrons transfer and photoresponse. The high PEC performance is surely due to the effect of Ni-MOF, which enhances the visible light absorption, together with the large surface area, efficient charge separation and high carrier mobility of the Ni-MOF/TDNR. Based on the analysis of experimental UV and visible optical responses, electrochemical impedance spectroscopy, and chrono-amperometry, a microscopic mechanism was proposed to explain the activity of these systems. The obtained results contribute to the investigation of MOF-sensitized OER photoanodes.

Figure 1. The schematic fabrication method of thin layer Ni-MOF nanostructures on TDNR and the mechanism of photoelectrochemical reaction for water splitting.

Characterization

Figure 2. The SEM images of bare TDNRs (A and B), and Ni-MOF/TDNRs (C and D)

Figure 3. The (A) XRD, (B) FTIR, (C) UV-Vis absorption spectra, and (D) Tauc plots of Ni-MOF/TDNR

PEC analysis

Figure 4. Chrono-amperometric measurements made on (blue) 0.005M Ni-MOF/TDNRs, (red) 0.01M Ni-MOF/TDNRs, (black) bare TDNRs, under chopped (left) and continuous (right) UV-Vis light irradiation.

Figure 5. Photo-electrochemical impedance spectroscopy diagrams measured under UV-vis (left) and Visible (right) light irradiation on 0.005M Ni-MOF/TDNRs, 0.01M Ni-MOF/TDNRs and bare-TDNRs.

Conclusions

Nanostructured photoelectrodes made of a mat of TiO₂ nanorods surface sensitized by Ni-MOF nanocoatings have been synthesized using a two-step method consisting of Ni electrodeposition followed by the solvothermal transformation into Ni-MOF. The Ni-MOFs were fully covered on the TDNRs and grown homogeneously with the layer thickness around 20nm~50nm on the surface of TiO₂ nanorods. The as-synthesized nanocomposites exhibit enhanced PEC performance and improved charges transfer after the successful combination of the Ni-MOF and TiO₂. This phenomenon promoted the oxygen evolution reaction in PEC system and was evaluated as a good photosensitizer as well. Hence, the high PEC performance was attributed to the presence of thin layer Ni-MOF, which enhances the visible light absorption, but also to the large surface area of the interface, that provides efficient charge separation and high carrier mobility. This novel nanocomposites (Ni-MOF/TDNRs) was attractive as a efficiently photoanode for water splitting in PEC system.

Reference

1. Duan, J., et al. (2017). "Ultrathin metal-organic framework array for efficient electrocatalytic water splitting." *Nat Commun* 8: 15341.
2. Yang, H., et al. (2019). "Metal-organic framework coated titanium dioxide nanorod array p-n heterojunction photoanode for solar water-splitting." *Nano Research* 12(3): 643-650.
3. El Rouby, W. M. A., et al. (2019). "Novel nano-architected water splitting photoanodes based on TiO₂-nanorod mats surface sensitized by ZIF-67 coatings." *International Journal of Hydrogen Energy* 44(59): 30949-30964.
4. El Rouby, W. M. A., et al. (2020). "Surface sensitization of TiO₂ nanorod mats by electrodeposition of ZIF-67 for water photo-oxidation." *Electrochimica Acta* 339: 135882.

Acknowledgement

The authors thank the Ministry of Science and Technology (MOST), Taiwan for the financial support under the grant. S.M. You also thank the Ministry of Education, Taiwan for financial support to University of Paris Saclay, France, the scholarship (International Talent Development Program) support under the grant No 1040082029B. Technical support from the characterization platform at ICMO in Paris-Saclay University is also gratefully acknowledged.