

The Progress of Photothermal Effect Enhanced Electrocatalytic Oxygen Evolution Reaction

Juan Wang*

School of Physical Science and Technology, Tiangong University, Tianjin 300387, China

Email: 2209576265@qq.com

Abstract

Harnessing light energy is an important means to alleviate the energy crisis and reduce environmental pollution. Light irradiation nanostructures can produce electromagnetic field enhancement, generate hot carriers, induce resonant energy transfer and photothermal effects. For oxygen evolution reaction from water splitting, the photothermal effect can serve to promote electrocatalytic activity and also adjust the reaction pathway, thus improving performance.

Keywords: photothermal effects; OER; water splitting.

1. Introduction

With the advancement of science and technology, the rise of human living standards, and the vigorous development of fossil fuels to promote economic development have brought about serious environmental problems, and the development of sustainable, non-polluting, high-performance new energy sources is imminent. A potential goal for developing new clean energy sources is to develop electrochemical conversion processes that convert macromolecules in nature into higher-value products through the coupling of renewable energy sources. Electrocatalysts can play a key role in energy conversion by improving the rate, efficiency and selectivity of chemical conversion[1].

Catalysts for photothermal coupled electrocatalysis can facilitate enhanced electrocatalytic performance by using light-induced local heating in the solar spectral range to generate high-energy hot carriers to initiate surface catalytic reaction pathways[2,3,4]. The electrochemical decomposition of water process is composed of two half-reactions, hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode, which easily yields high purity hydrogen and is the most environmentally friendly way to prepare green hydrogen. However, the oxygen precipitation reaction at the anode is a complex four-electron transfer process with slow reaction kinetics and requires overcoming a high reaction potential, which severely limits the efficiency of hydrogen production [5,6]. To date, the noble metals Ru and Ir are the most effective catalysts for oxygen precipitation reactions[7].

* Corresponding author.

however, the high cost and scarcity of noble metals limit the large-scale application of electrolytic water hydrogen production technology, so efforts have been devoted to the development of low-cost, highly active, and stable catalysts for oxygen precipitation reactions in electrolytic water[8]. Heating systems are commonly introduced in industrial water electrolysis processes, and the additional thermal energy can also accelerate the reaction kinetics, promote the oxygen adsorption and desorption process, reduce the activation energy, and enhance the performance of electrolytic water. However, heating systems often require large, complex equipment to operate. Photothermal conversion materials coupled with electrocatalysts that can convert light into heat in a specific range are an effective way to enhance electrocatalytic performance in electrolytic water processes, which can be achieved by in situ local heating under visible or near-infrared light irradiation only, without the need for external devices and avoiding the influence of electrolyte temperature[9].

In this paper, the application of photothermal effect in electrocatalytic oxygen precipitation reaction and its mechanism are reviewed.

2. Application of photothermal effect in electrocatalytic oxygen precipitation reaction and its mechanism

Lunhong Ai's group[10] reported a Fe-tannic coordination network (Fe-TAN) nanoparticles covered on the photothermally active iron foam (O-IF) to enhance OER performance under irradiation of NIR laser(Figure 1). The heat localization induces surface temperature of Fe-Tan/O-IF rapidly increases from room temperature to 53.5 °C within 4 min irradiation of 4.26 W NIR laser due to the wide and intense light absorption. Under NIR light irradiation, the Fe-Tan/O-IF electrode provides a current density of 10 mA cm⁻² at an overpotential of 302 mV, which is 22 mV lower than the current density without illumination.

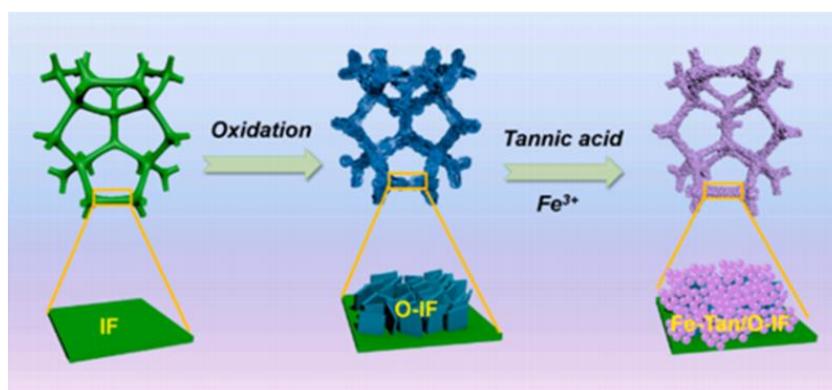


Figure 1: Schematic illustration of fabrication procedure of Fe-Tan/O-IF electrode.

Heqing Jiang's group[11] constructed the multifunctional reduced graphene oxide (rGO) film with broad light absorption, which can maximize the use of solar light for generating localized heat that speeds up the transfer of electron and mass in the electrocatalytic OER process(Figure 2). The introduction of solar energy greatly improved the catalytic performance of OER. Compared with dark, at 10 mA cm⁻², the overpotential decreases from 308 mV to 215 mV, and the Tafel slope rate decreases from 156.7 mV dec⁻¹ to 94.3 mV dec⁻¹. This work represents the first example that solar light-assisted technologies are applied on free-standing multifunctional carbon-based catalysts over a wide range of solar spectrums for maximizing their OER activity.

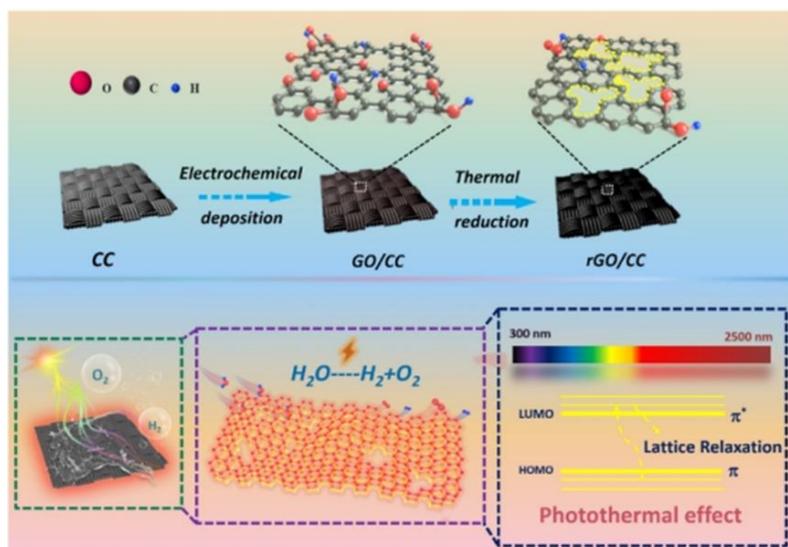


Figure 2: Schematic illustration of the synthesis of rGO/CC for broad spectrum solar-enhanced oxygen evolution reaction.

Isabel C. de Freitas and his colleagues [12] developed an Au-IrO₂ nanoflower structure for oxygen evolution reaction. Under LSPR excitation, the overpotential decreased from 326 mV to 286 mV. Through DFT theoretical calculation and analysis showed that $\Delta G(O^*) - \Delta G(OH^*)$ for IrO₂/Au (1.30 eV) was higher than for IrO₂ (1.19 eV). The increase in the value of $\Delta G(O^*) - \Delta G(OH^*)$ brings it closer to the maximum of the volcano plot. Furthermore, when hot holes are LSPR-excited in the Au NPs and then transferred to O* (or the Ir-O antibonding state), the charge lowers the binding energy of O* increasing the value of $\Delta G(O^*)$, and thus increases the OER activity. It is plausible that the hot holes may also lower the binding energy of OH*. However, because OH* has much less available states to populate the holes, this weakening of the binding energy of OH* is much less than the O* binding, which overall makes $\Delta G(O^*) - \Delta G(OH^*)$ more positive under LSPR excitation, further shifting this value closer towards the maximum point in the volcano plot between $\Delta G(O^*) - \Delta G(OH^*)$ and the OER activity. Bin Zhang's group [13] present a photothermal-effect-driven strategy to promote the electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities of nickel/reduced graphene oxide (denoted as Ni/RGO) bifunctional electrocatalysts. Ni serves as active component for electrocatalytic reactions, and RGO absorbed incident light to heat the supported active species and ameliorate the conductivity of electrocatalyst. After illumination, the OER and HER activities of Ni/RGO significantly increased, the overpotentials of HER and OER decreased by 49 mV (233 mV to 184 mV) and 50 mV (410 mV to 360 mV) at 10 mA cm⁻² current density, respectively. The main reason for the enhanced electrocatalytic performance is that RGO absorbs incident light to load hot active species, which ameliorate the electron transfer process and hence improve conductivity, and thermally active species can heat the supported nickel nanoparticles and nickel-based oxides for HER and OER, promoting the thermodynamics and dynamics of OER and HER. Jing Qi and his colleagues [14] prepared a carbon hemisphere-supported Co(OH)₂ and MoS₂ with strong light absorption ability as OER and HER catalysts respectively. The two hybrids showed enhanced electrocatalytic activity of water splitting under light irradiation, owing to the elevated local temperature of carbon that had been heated by the light. Zhiqun Lin's Group [15] report an integrated operando Raman and

density functional theory (DFT) plus Hubbard U (DFT + U) study to exercise and unveil the light-to-thermal conversion of inverse spinel oxide nanoparticles (NPs) in promoting the generation of dynamic active sites via surface reconstruction into oxyhydroxides and thus greatly enhancing their OER activity. Upon the near-infrared light irradiation, the photothermal heating of the NFO-based electrode progressively raises the temperature, accompanied by a marked decrease of overpotential. Accordingly, only an overpotential of 309 mV is required to yield a high current density of 100 mA cm^{-2} , greatly lower than recently reported earth-abundant electrocatalysts. By operating Raman spectroelectrochemistry, it was shown that under 808 nm near-infrared radiation, due to the semiconducting properties of NFO NPs, which can absorb and respond to near-infrared light, the hot holes generated on the surface of NFO NPs can reduce the energy barrier of Ni^{2+} to Ni^{3+} and facilitate the surface reconstruction into more electrocatalytic active $\gamma\text{-NiOOH}$. The thermal energy generated by photothermal conversion can accelerate the activation of reactant molecules during the electrocatalytic process, making it easier to overcome the activation barrier, thereby improving the electrocatalytic reaction kinetics. Lunhong Ai and his colleagues [16] report a robust photothermal–electrocatalytic water splitting system based on broadband solar harvesting nickel phosphide (Ni_2P) within a heat-insulating quasi-Ni-BDC-MOF. Benefiting from the controllable thermal treatment for partial deligandation and synchronous phosphorization, the highly dispersed ultrafine Ni_2P nanoparticles are spatially confined within quasi-Ni-BDC-MOF nanosheets, ensuring the effective utilization of local heat assisted by heat-insulating quasi-Ni-BDC-MOF to suppress heat loss. The resulting black $\text{Ni}_2\text{P}@$ quasi-Ni-BDC exhibits an ultrasensitive and stable light-to-heat response under simulated solar light illumination. By coupling with this excellent photothermal performance, $\text{Ni}_2\text{P}@$ quasi-Ni-BDC under full spectrum light illumination demonstrates the ultralow overpotentials of 246 and 218 mV to deliver 100 mA cm^{-2} current density for oxygen and hydrogen evolution reactions and shows negligible degradation over operating for 50 h and excellent recyclability under several repeated on–off cycles. Xiaojun Zeng and his colleagues [17] report an effective cation exchange strategy to embed Fe^{3+} ions in amorphous TiO_2 nanoshells followed by nitridation to synthesize unique mesoporous Fe_2N -embedded TiO_xN_y nanoshells (Figure 3). The optimized mesoporous Fe_2N -embedded TiO_xN_y nanoshells show considerable OER activity with an overpotential of 270 mV to reach 10 mA cm^{-2} , outperforming the commercial RuO_2 catalyst. This work represents the unique report on plasmon-excited TiN-induced hot electrons for successfully activating the OER catalysis.



Figure 3: Schematic for the synthetic process of mesoporous Fe_2N -embedded TiO_xN_y nanoshells.

Xing-Hua Xia's group [18] propose a plasmon-activated OER electrochemical system of AuNRs/NiCo-MOFs. The AuNRs are decorated onto the surfaces of ultrathin 2D NiCo-MOFs. The catalytic activity of NiCo-MOFs can be considerably enhanced upon LSPR excitation of AuNRs due to the efficient injection of holes from AuNRs to NiCo-MOFs. This process greatly facilitates the formation of high valence Ni^* species in NiCo-

MOFs with better matched energy levels for the OER. The electrons could transfer from the low unoccupied molecular orbital (LUMO) of NiCo-MOFs to AuNRs, resulting in a decreased energy level of NiCo-MOFs (Figure 4). Benefiting from these factors, a highly efficient OER performance at a low potential could be achieved, the AuNRs/NiCo-MOF hybrid exhibits superior electrocatalytic activity for the OER with a decreased overpotential from 283 to 240 mV at 10 mA cm⁻², and a reduced Tafel slope from 83 to 69 mV dec⁻¹. Such LSPR enhanced OER electrocatalysis is also observed in Co-MOFs, indicating the generality of the concept of plasmon enhanced electrocatalysis of pristine MOFs.

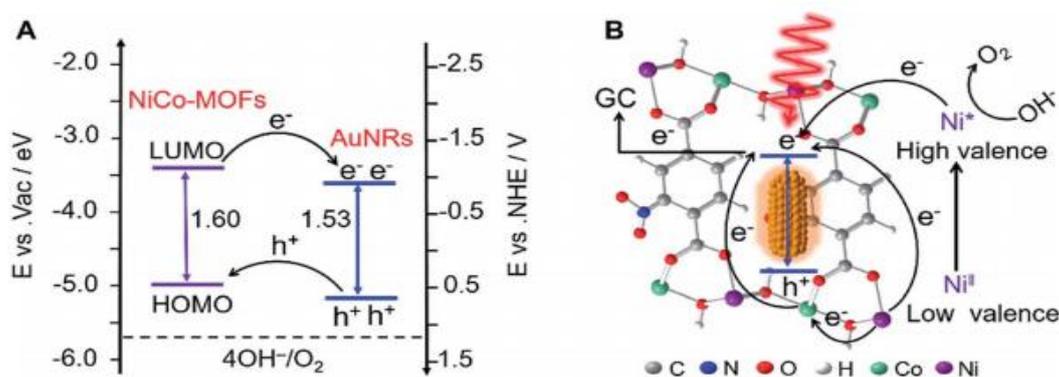


Figure 4: Mechanism of the plasmon enhanced OER. (A) AuNRs/NiCo-MOFs and the energy level diagram showing the transfer processes of hot charge carriers between AuNRs and NiCo-MOFs. (B) Schematic electron transfer paths occurring between AuNRs and NiCo-MOFs under 808 nm light irradiation.

Shihe Yang's group[19] used CuS nanodisks electrocatalysts for OER with excellent performance. The catalyst has an obvious LSPR peak in the near-infrared region, and the OER overpotential and Tafel slope decrease with the change of illumination wavelength. The OER performance of the CuS nanodisks electrocatalyst is significantly improved within 60 min, especially the samples uploaded onto the NiFe LDH electrode have ultra-low values of η_{50} (215 mV) and η_{100} (262 mV). Under illumination, near-infrared light irradiation can generate a large number of hot holes on the surface of CuS, and the hole density in the samples under different irradiation conditions is completely different, which is highly dependent on the illumination wavelength. Typically OER involves the adsorption of oxygen-containing species at the active site, followed by continuous surface chemical transitions with four-electron release, and hot holes can react with electrons, hot holes are injected into the CuS nanodisks, reducing these steps reaction barrier, thereby promoting the entire OER reaction. Xueqin Liu's group[20] prepared a Co-based bifunctional catalyst for oxygen evolution reaction, and the electrocatalytic performance of Co₃O₄ can be significantly improved by the photothermal effect. Under the irradiation of 808 nm near-infrared light, when the power density was increased from 1 W cm⁻² to 3 W cm⁻², 5 W cm⁻², the temperature could be increased to 63.1 °C, and the current at 10 mA cm⁻² At density, the overpotential of Co₃O₄ is 253 mV and the Tafel slope is 74.6 mV dec⁻¹ (Figure 5), which is due to the accelerated electron transfer, good reactive electrochemistry and large active specific surface area and Enhanced bubble evolution and therefore higher OER performance. Besides, CoN, CoP, and CoS exhibit stronger catalytic performance due to better photothermal effect, and metal-doped Co-based catalysts can also further improve OER performance through photothermal effect assistance.

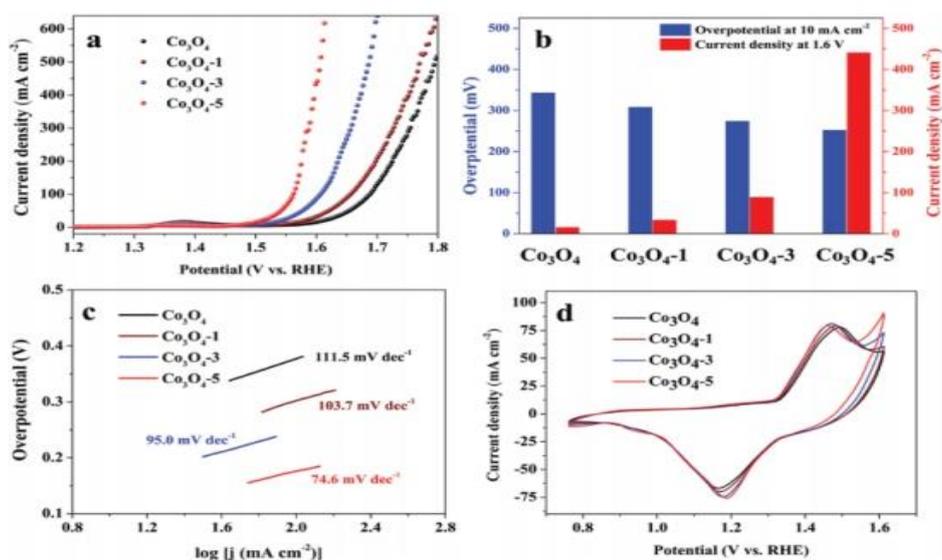


Figure 5: (a) LSV polarization curves, (b) comparison of the overpotential at current density of 10 mA cm^{-2} and the current density at 1.6 V , (c) Tafel plots, and (d) CV curves of Co_3O_4 , $\text{Co}_3\text{O}_4\text{-1}$, $\text{Co}_3\text{O}_4\text{-3}$, and $\text{Co}_3\text{O}_4\text{-5}$ electrodes.

3. Conclusion

In summary, through the unremitting efforts of researchers, the following conclusions have been reached: the photothermal effect introduced into the electrolytic water oxygenation reaction system can effectively reduce the overpotential of the oxygenation reaction, accelerate the reaction kinetics, reduce the activation energy and increase the current density.

Acknowledgements

References

- [1] Seh Z W, Kibsgaard J, Dickens C F, et al. Combining theory and experiment in electrocatalysis: Insights into materials design[J]. *Science*, 2017, 355(6321): eaad4998.
- [2] Ma R, Sun J, Li D H, et al. Review of synergistic photo-thermo-catalysis: Mechanisms, materials and applications[J]. *International Journal of Hydrogen Energy*, 2020, 45(55): 30288-30324.
- [3] Mateo D, Cerrillo J L, Durini S, et al. Fundamentals and applications of photo-thermal catalysis[J]. *Chemical Society Reviews*, 2021, 50(3): 2173-2210.
- [4] Kho E T, Tan T H, Lovell E, et al. A review on photo-thermal catalytic conversion of carbon dioxide[J]. *Green Energy & Environment*, 2017, 2(3): 204-217.
- [5] Stevens M B, Enman L J, Batchellor A S, et al. Measurement techniques for the study of thin film heterogeneous water oxidation electrocatalysts[J]. *Chemistry of Materials*, 2017, 29(1): 120-140.
- [6] Song J, Wei C, Huang Z F, et al. A review on fundamentals for designing oxygen evolution electrocatalysts[J]. *Chemical Society Reviews*, 2020, 49(7): 2196-2214.
- [7] Shi Q, Zhu C, Du D, et al. Robust noble metal-based electrocatalysts for oxygen evolution reaction[J].

- Chemical Society Reviews, 2019, 48(12): 3181-3192.
- [8] Zhang H X, Li Y, Li M Y, et al. Boosting electrocatalytic hydrogen evolution by plasmon-driven hot-electron excitation[J]. *Nanoscale*, 2018, 10(5): 2236-2241.
- [9] Shi F, He J, Zhang B, et al. Plasmonic-enhanced oxygen reduction reaction of silver/graphene electrocatalysts[J]. *Nano letters*, 2019, 19(2): 1371-1378.
- [10] Synergistically boosting oxygen evolution performance of iron-tannic electrocatalyst via localized photothermal effect; *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 638 (2022) 128248
- [11] Liang Y, Zhang Y, Wang X, et al. Multifunctional reduced graphene oxide film as electrocatalysts and photothermal layer for broad spectrum solar-enhanced oxygen evolution reaction[J]. *Materials Today Energy*, 2022, (100966): 1-8.
- [12] Design-controlled synthesis of IrO₂ sub-monolayers on Au nanoflowers: marrying plasmonic and electrocatalytic properties; *Nanoscale*; 10.1039/d0nr01875a Zhang, X.; Gao, B.; Creamer, A. E.; Cao, C.; Li, Y., Adsorption of VOCs onto engineered carbon materials: A review. *J Hazard Mater* **2017**, 338, 102-123.
- [13] Gu L, Zhang C, Guo Y, et al. Enhancing electrocatalytic water splitting activities via photothermal effect over bifunctional nickel/reduced graphene oxide nanosheets[J]. *ACS Sustainable Chemistry & Engineering*, 2019, 7(4): 3710-3714.
- [14] Qi J, Zhang W, Cao R. A new strategy for solar-to-hydrogen energy conversion: Photothermal-promoted electrocatalytic water splitting[J]. *ChemElectroChem*, 2019, 6(10): 2762-2765.
- [15] Gao L, Cui X, Wang Z, et al. Operando unraveling photothermal-promoted dynamic active-sites generation in NiFe₂O₄ for markedly enhanced oxygen evolution[J]. *Proceedings of the National Academy of Sciences*, 2021, 118(7): e2023421118.
- [16] Ai L, Li N, Chen M, et al. Photothermally boosted water splitting electrocatalysis by broadband solar harvesting nickel phosphide within a quasi-MOF[J]. *Journal of Materials Chemistry A*, 2021, 9(30): 16479-16488.
- [17] Zeng X, Choi S M, Bai Y, et al. Plasmon-Enhanced Oxygen Evolution Catalyzed by Fe₂N-Embedded TiO_xN_y Nanoshells[J]. *ACS Applied Energy Materials*, 2019, 3(1): 146-151.
- [18] Hu W C, Shi Y, Zhou Y, et al. Plasmonic hot charge carriers activated Ni centres of metal-organic frameworks for the oxygen evolution reaction[J]. *Journal of Materials Chemistry A*, 2019, 7(17): 10601-10609.
- [19] Huang M, Wang X, Xing G, et al. Plasmonic Hot Hole Extraction from CuS Nanodisks Enables Significant Acceleration of Oxygen Evolution Reactions[J]. *The Journal of Physical Chemistry Letters*, 2021, 12(33): 7988-7996.
- [20] Jin B, Li Y, Wang J, et al. Promoting Oxygen Evolution Reaction of Co-Based Catalysts (Co₃O₄, CoS, CoP, and CoN) through Photothermal Effect[J]. *Small*, 2019, 15(44): 1903847.