

Surface strategies towards artificial photocatalytic Z-Scheme overall water splitting with wide visible light utilization

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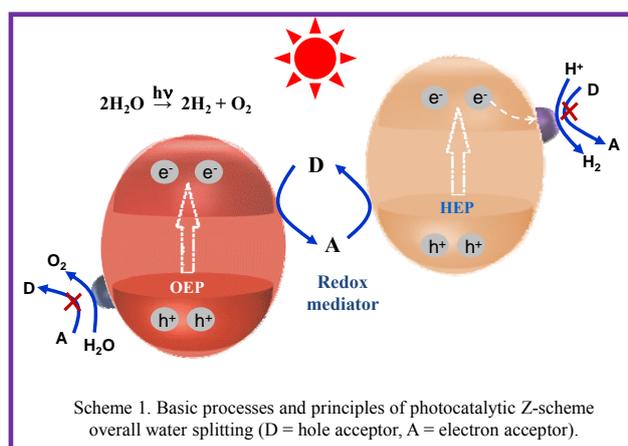
Abstract: Solar water splitting for hydrogen production by particulate artificial photosynthesis is one of the promising ways to convert solar energy into chemical one. Here we will give a brief summary on our recent research progress on the fabrication of effective Z-scheme overall water splitting systems using wide visible-light-responsive materials with an emphasis on the surface modification strategies. Some typical examples will be introduced to address the key issues of artificial photosynthesis such as light harvester, charge separation and surface catalysis etc. Meanwhile the interface effect during the surface modification is also highlighted.

Keywords: photocatalysis, water splitting, surface modification.

1. Introduction

Global warming and energy crisis have stimulated research activities towards the development of renewable and clean energy sources. Solar energy is a principle source of sustainable energy. In spired by natural photosynthesis of plants that transforms CO₂ and H₂O into carbohydrates and O₂ at room temperature under sunlight, extensive research activities have been devoted to developing artificial photosynthesis for harvesting diffuse and intermittent sunlight, and converting it to solar fuels that can be stored and transported. Overall water splitting (OWS) with water as an electron donor is one of the key processes in this field.^[1]

Solar water splitting over semiconductor involves such basic processes as light absorption, charge separation and catalytic reaction etc., and the STH conversion efficiency is an integral result of above three processes. If the efficiency of each step is separately calculated, the STH efficiency will be the production of above three efficiencies.^[2] It can be described as follows: $\eta_{\text{STH}} = \eta_{\text{LA}} \times \eta_{\text{CS}} \times \eta_{\text{CR}} \times 100\%$ (η_{LA} : efficiency of light absorption; η_{CS} : efficiency of charge separation; η_{CR} : efficiency of catalytic reaction). On the basis of the calculation formulation, the efficiency of light absorption is crucial in determining the theoretical maximal STH efficiency, given that efficiencies of both charge separation and catalytic reaction is unity. Normally, the efficiency of light absorption is in essence determined by the absorption edge of the photocatalyst which is related to the band gap of semiconductor. It is general to know that the longer the absorption edge is, the bigger the theoretical STH efficiency is. As a result, it is extremely desirable to use



the material with wide visible light utilization. However, if the absorption edge of one material is extended, its driving force for charge separation and surface reaction will be decreased. Thus, controllable structure modification and synthesis should be made towards the goal. Besides the challenges of charge separation and surface reaction caused by the decreased driving force, another challenge in fabricating Z-scheme overall water splitting is to confront the competing reaction of shuttle ions.^[3] As given in the scheme 1, the water reduction and oxidation is competed with the reduction and oxidation of shuttle ions

respectively.

In this talk, we will introduce some effective surface strategies to address such challenges, among which the fabrication of heterostructures, coating of cocatalysts (single or dual ones) as well as interface engineering will be adopted. Based on our efforts, successful construction of Z-scheme overall water splitting systems as well as significant promotion of water splitting efficiency has been achieved.

2. Experimental

The nitrogen-containing photocatalysts were synthesized by nitriding the corresponding oxides under the flow of ammonia at high temperature, and the oxide-based photocatalysts were synthesized by thermal process. The photocatalytic activities were evaluated by using 300 W Xe lamp and connecting a vacuum system and cooling water system.

3. Results and discussion

Here we prepared the $\text{MgTa}_2\text{O}_{6-x}\text{N}_y/\text{TaON}$, $\text{BaTaO}_2\text{N}/\text{Ta}_3\text{N}_5$ heterostructures for promoted charge separation as well as H_2 -evolving photocatalysts, based on which Z-scheme overall water splitting systems can be constructed.^[4-5] Secondly, we developed an efficient method to deposit the CoO_x cocatalyst towards highly efficient water oxidation on Ta_3N_5 or LaTiO_2N .^[6-7] Meanwhile, we demonstrated that the interface engineering of magnesia is favorable for more homogeneous dispersion of coated CoO_x as well as promoted charge separation. Additionally, the interface magnesia modification is found to favor the inhibition of competing reaction of I^- ions that was used for construction of Z-scheme OWS.^[8] Finally, we introduce the selective deposition of dual cocatalyst on the surface of BiVO_4 with spatial separation of electrons and holes among facets.^[9-10] Based on this, we can significantly promote the O_2 evolution rate of BiVO_4 as well as fabricate a OWS system with apparent quantum efficiency of above 10% at 420 nm.

4. Conclusions

Surface strategies have been demonstrated to be efficient for promotion of charge separation and/or surface catalysis, based on which the H_2 or O_2 -evolving rate can be remarkably promoted. The interface engineering is demonstrated to favor the dispersion of cocatalysts or inhibit competing reaction. The promotion of H_2 and O_2 -evolving reaction kinetics and effective inhibition of competing reactions caused by shuttle ions are demonstrated to be the key parameters for construction of Z-scheme OWS systems.

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