Spatial Charge Separation on Semiconductor-based Photocatalysts for Photocatalytic Water Splitting

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Abstract: Spatial separation of photogenerated charges is one of the most critical factors in photocatalysis. Recently, we reported that the spatial charge separation can take place between different facets of semiconductor-based photocatalysts ($BiVO_4$, Cu_2O, $SrTiO_3$ etc.), which is a unique strategy for charge separation differing from the "junction" strategy. Following these findings, we rationally constructed the reduction and oxidation cocatalysts on the different facets of photocatalysts and the photocatalytic activity was found to be greatly enhanced. Spatial charge separation between different facets has been demonstrating to be a general strategy for constructing efficient photocatalyst systems for solar energy conversion.

Keywords: Charge separation, cocatalyst, photocatalytic water splitting.

1. Introduction

Charge separation is a challenging and long-standing issue in photocatalysis. Many useful strategies for improving charge separation have been explored extensively, for example, constructing p-n junction or heterojunction between two semiconductors based on the differences of their Femi levels; constructing a phase-junction between two difference phases of a semiconductor (anatase and rutile phases TiO_2, α and β phases Ga_2O_3 etc.). However, it is still unknown how the spatial charge separation take place on a single semiconductor. In our group, we reported that the photogenerated electrons and holes can be spatially separated onto different facets of semiconductor-based photocatalysts ($BiVO_4$, Cu_2O, $SrTiO_3$ etc.), which is a unique strategy for charge separation differing from the "junction" strategy. Following these findings, we can rationally construct the reduction and oxidation cocatalysts on the different facets, which was found to greatly improve the charge separation and inhibit the charge recombination.

2. Experimental

Semiconductor-based crystals ($BiVO_4$, Cu_2O, $SrTiO_3$ etc.) with regular morphologies and specific exposed facets were synthesized by a hydrothermal procedure. For the facet-selective photo-depositions, three ways containing single reduction, single oxidation as well as simultaneous reduction and oxidation were carried out at room temperature without pH value adjusted. Normally, photocatalyst powder and a calculated amount of metal precursors were mixed in demonized water. The suspension was then irradiated by a 300 W Xe lamp under continuous stirring. The photocatalytic overall water splitting reactions were carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp (Ushio-CERMAXLX300). Before irradiation, the reaction system was thoroughly degassed by evacuation in order to drive off the air inside. The amount of evolved H_2 and O_2 was determined by an on-line gas chromatograph (Agilent, GC-7890, TCD, Ar carrier).

3. Results and discussion

The *in-situ* photo-deposition method was used to probe the sites for photogenerated electrons and holes. Taking $BiVO_4$ as an example, we chose photo-reduction deposition of noble metals and photooxidation deposition of some metal oxides as the reduction and oxidation probes, respectively. It was found that the photo-reduction of noble metals (Au, Pt and Ag) are selectively deposited on {010} facets, while the photo-

oxidation deposition of metal oxides (MnO_x and PbO_2) only takes place on {110} facets, which indicates that the photogenerated electrons and holes are separated on {010} and {110} facets, respectively (Figure 1). Based on this finding, the reduction cocatalysts and oxidation cocatalysts can be rationally deposited on different facets by photo-deposition method. Interestingly, we found that the photocatalytic water oxidation activity can be greatly enhanced to more than 100 times when the reduction and oxidation cocatalysts are selectively deposited on the different facets, showing a remarkable synergistic effect of the dual-cocatalysts. Considering whether the spatial charge separation can take place on a semiconductor-based crystal with high symmetry structure (e.g., cubic phase). Recently, taking cubic phase $SrTiO_3$ as photocatalyst, we designed and synthesized $SrTiO_3$ nanocrystals from isotropic facets (6-facet $SrTiO_3$) to anisotropic facets (18-facet $SrTiO_3$). We found that the reduction and oxidation active sites can only be separately distributed on the anisotropic facets of 18-facet $SrTiO_3$ nanocrystals, but randomly distributed on every facet of 6-facet $SrTiO_3$ nanocrystals. The selective distribution of dual-cocatalysts on anisotropic facets of $SrTiO_3$ nanocrystals results in a remarkable synergetic effect for photocatalytic overall water splitting and leads to a five-fold enhancement of the apparent quantum efficiency (Figure 1). The superior performance can be attributed not only to the charge separation between anisotropic facets, but also to the synergetic effect between the facet charge separation and the spatially separated reduction and oxidation active sites.

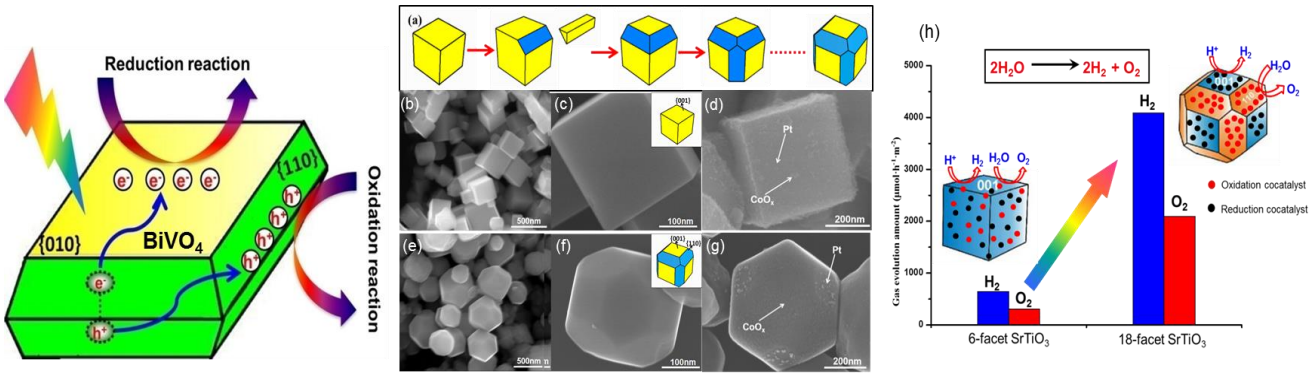

Figure 1. The scheme of spatial charge separation between different facets of $BiVO_4$ and $SrTiO_3$ crystals.

4. Conclusions

In summary, we have demonstrated that the spatial charge separation can take place between different facets of semiconductor-based photocatalysts ($BiVO_4$, Cu_2O, $SrTiO_3$ etc.), which is a new finding of charge separation, differing from the traditional "junction" between two different materials. Based on the principle, we rationally constructed the reduction and oxidation cocatalysts on different facets so that the reduction and oxidation reactions are spatially separated, which can greatly enhance the activity for photocatalytic water splitting. The findings of spatial charge separation should be intriguing for understanding the mechanism of photocatalytic reactions, and designing solar energy devices for high efficient conversion of solar energy.

References

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