Research Report

Development of High-Performance Materials for Eco-Friendly Energy Conversion Processes
- Visible Light Responding Photocatalyst for Water Splitting -

Nowadays, the world is facing serious environmental problems such as global warming, acid rain, photochemical pollution which mainly originate from the production and usage of fossil fuels. Therefore, it is very urgent to develop a clean and sustainable energy system to solve such problems. One possibility is photocatalysis for water splitting to produce clear hydrogen energy. In this micro review, I will introduce fundamentals and up-to-date developments of visible-light-responding photocatalysts for water splitting.

Introduction

Nowadays, the world is facing serious environmental problems. Many environmental problems, such as greenhouse effect, acid rain and photochemical pollution originated from the production and usage of fossil fuels. So it is very urgent to develop a clean and sustainable energy system to solve such problems. There are at least two ways to solve such problems. In one way, we have to optimize the conventional energy utilization system. For example, coal gasification by using catalysts has been developed for power plant for reducing the CO₂ production. In another way, we have to develop new energy systems, such as solar-hydrogen system, to substitute the fossil fuels. In both approaches of eco-friendly energy conversion, development of high-performance materials processes is very critical, and my research is concerned with (1) investigation and development of inorganic materials to facilitate coal gasification and (2) investigation and development of novel visible-light-responding photocatalysts for VOC removal and water splitting.

In this micro review, I will focus on visible-light-responding photocatalysts for water splitting.

Fundamentals of photocatalytic water splitting

Photocatalytic water splitting ¹, so called Honda-Fujishima effect, was discovered more than 30 years ago. In this process, light energy is transformed to chemical energy as H₂ energy when H₂O is decomposed to H₂ and O₂ by using light energy. So the reaction of photocatalytic water splitting is called as artificial photosynthesis.

Water splitting as shown in equation 1 is difficult to take place because of 237 kJ/mol of Gibbs free energy.

$$\text{H}_2\text{O(l)} \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$$  \hspace{1cm} (1)

To achieve splitting water, photon of 1.23 eV, the theoretical minimum energy requirement corresponding to light of about 1100 nm, will be absorbed by photocatalysts to excite an electron from valence band to conduction band. Considering the hydrogen overpotential, 1.8 eV of photon was suggested to use for water splitting ².

Besides, the bottom level of the conduction band has to be more negative than the redox potential of H⁺/H₂ (0 V vs. NHE), while the top level of the valence band has to be more positive than the redox potential of O₂/H₂O (1.23 V) as shown in Fig 1.

Main processes in a photocatalytic reaction are shown in Fig. 2. The first step (i) of the photocatalytic reaction is absorption of photons to form electron-hole pairs in the photocatalyst. The band gap of a photocatalyst should be wider than 1.8 eV to meet the requirement of water splitting as mentioned above. At the same time,
for visible-light-responding photocatalyst, the band gap should be narrower than 3.0 eV to absorb visible light ($\lambda > 420$ nm). Moreover, the conduction and valence band positions should satisfy the energy requirements set by the reduction and oxidation potentials for H$_2$O, respectively. Therefore, it is very difficult to design photocatalysts for water splitting under visible light.

After absorbing photon, photogenerated carriers separate and migrate to surface of photocatalysts (step ii). The crystal structure and the crystallinity strongly affect these processes. The defects in the crystal work as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the photocatalytic activity. Therefore, a high degree of crystallinity with a less amount of the defects, rather than a high surface area, is required of photocatalysts, especially for an uphill reaction like water splitting.

The final step (iii) consists of the surface chemical reactions. The important points for this step are surface character (active sites) and quantity (surface area). Cocatalysts such as Pt, NiO, and RuO$_2$ are usually loaded to introduce active sites for H$_2$ evolution because the conduction band levels of many oxide photocatalysts are not high enough to reduce H$_2$O to produce H$_2$ without catalytic assistance. Active sites for 4-electron oxidation of H$_2$O are required for O$_2$ evolution. Although this reaction is demanding, cocatalysts are unnecessary for oxide photocatalysts because the valence band is deep enough to oxidize H$_2$O to form O$_2$.

**Short survey of development of visible-light-responding photocatalysts**

Up to date, a lot of photocatalysts were discovered by researchers, but many of them only work under UV light, which occupy only 4% of solar energy. In order to take advantage of much more solar energy, visible-light-driven photocatalysts becomes more and more important. However, a few photocatalysts can stoichiometrically split water into hydrogen and oxygen under visible light up to date. Many visible-light-driven photocatalysts produced either hydrogen or oxygen from sacrificial reagent solution due to unsuitable conduction band or valence band. So it is necessary and useful to discuss development of visible-light-responding photocatalysts for overall water splitting from a view point of designing new materials.

**1. Synthesis of oxide photocatalysts**

Recently, some new oxide photocatalysts were synthesized such as InMO$_4$ ($M=V^{5+}$, Nb$^{5+}$, Ta$^{5+}$) 5-11, AMn$_2$O$_4$ ($A=$Cu, Zn) 12, 13, AlInO$_4$ ($A=Li, Na$) 14 and so on. However, those materials only produced H$_2$ or O$_2$ from sacrificial reagent solution under visible light irradiation.
2. Non-metal doping to TiO$_2$

The development of oxide photocatalysts have been almost exclusively investigated from the combination and substitution of metal cations. Non-metal doping to TiO$_2$ was firstly proved by R. Asahi et al. to be an effective way to make photocatalysts responsible to visible light. After N-doping, TiO$_2$ decomposes methylene blue and gaseous acetaldehyde under visible light ($\lambda < 500$ nm). Three requirements should be satisfied to realize visible light response. Firstly, doping should produce states in the band gap of TiO$_2$ to absorb visible light; Secondly, the conduction band, including subsequent impurity states, should be as high as that of TiO$_2$ or higher than the H$_2$/H$_2$O level to ensure its photoreduction activity; finally the states in the gap should overlap sufficiently with the band states of TiO$_2$ to transfer photoexcited carriers to reactive sites at the catalyst surface within their lifetime. However, N-doping TiO$_2$ cannot be applied to overall water splitting.

3. Oxynitride photocatalyst

Recently, GaN:ZnO oxynitride solid solution was discovered as visible-light-responding photocatalyst for overall water splitting. This material has wurtzite-type crystal structure. After loading RuO$_2$, it can split H$_2$O into H$_2$ and O$_2$ under visible light ($\lambda < 460$ nm). Quantum efficiency was 0.14% in the range of 300 nm and 480 nm. The calculation of density functional theory showed that the bottom of conduction band consisted of Ga 4s and 4p orbitals and the top of valence band came from the N2p and Zn3d orbital, repulsion of which make the band gap of the oxynitride solid narrow to absorb visible light. GaN:ZnO also proved that formation of solid solution was an effective method to adjust the band gap of materials.

4. Z-scheme photocatalysis systems

Z-scheme photocatalytic system (Fig. 3) was reported firstly by Sayama et al. to achieve overall water splitting by using IO$_3$/I$^-$ redox couple, which responded to visible light up to 450 nm. In this system, SrTiO$_3$: Cr and WO$_3$ were used as photocatalysts for producing H$_2$ and O$_2$ respectively. Besides those photocatalysts, BiVO$_4$, Bi$_2$MoO$_6$, and TaON can be used for H$_2$ production and Rh-doped SrTiO$_3$ for O$_2$ production. The quantum efficiency of Z-scheme photocatalytic systems is still low (< 0.3%) because of usage of redox couple. However this system has one advantage that H$_2$ and O$_2$ can be separately produced to avoid possibility of explosion comparing to normal H$_2$-O$_2$-mixture system.

5. Band engineering

For overall water splitting under visible light, the band gap of photocatalyst should meet to the redox potential of water and be smaller than 3 eV to absorb visible light ($\lambda > 420$ nm). In general, the valence band of oxide photocatalyst was consisted of O2p orbital (ca. +3 eV). At the same time, conduction band of photocatalysts should be higher than 0 eV for reducing water. Since most of oxide photocatalysts for overall water splitting hardly absorbed visible light, adjustment of the band structure of photocatalysts is one of major strategies for developing new materials. This method was called as the band engineering. The purpose of band engineering is to use donor level or new valence band with higher potential than O2p to narrow the band gap as shown in Fig. 4. In three types of band engineering, the formation of a solid
solution is the most promising way to develop a new photocatalyst because the simultaneous adjustment of conduction and valence bands is possible.

Developments of visible-light-responding photocatalysts for overall water splitting in my research

As mentioned above, many new photocatalysts were discovered to have the ability of absorbing visible light, but most of them are active to produce either H₂ or O₂ with sacrificial reagents. In order to split water to H₂ and O₂ under visible light, the conduction band and valence band of a photocatalyst should meet the potential requirements of reduction and oxidation of H₂O at the same time. Band engineering by the formation of a solid solution was reported to be a feasible and effective method to obtain suitable conduction band and valence band for splitting water \(^{16, 21}\). I focused on BiVO₄ and BiₓWO₆ \(^{22-24}\) which were reported to be visible-light responding but inactive for overall water splitting. In my study, BiYWO₆ and BiₓY₁₋ₓVO₄ solid solutions were synthesized and found that they could split water under visible light.

BiYWO₆ (BYW), a solid solution of BiₓWO₆ (BW) and Y₂WO₆ (YW), was found to be a new photocatalyst for overall water splitting under visible light irradiation. The band gap of BYW was 2.71 eV and it absorbed visible light up to 470 nm shown in Fig. 5. The loading of cocatalysts such as RuO₂ and Pt-Cr₂O₃ was indispensable to photocatalytically split water, and the best performance was observed with 0.5 wt% RuO₂/BYW: under irradiation of visible light (λ > 420 nm) to the reaction system of 100 mL H₂O and 0.5 g catalyst, amounts of the produced hydrogen and oxygen were about 12.3 and 5.6 μmol in each 3 h, respectively. Since both end materials of BW and YW were inactive for the photocatalytic water splitting, the formation of the solid solution was proven to be the feasible method to obtain visible-light-driven photocatalyst through the adjustment of position of conduction and valence bands of the oxide.

Fig. 4
Three types of band engineering for the design of visible-light-driven photocatalysts.

Fig. 5
Diffuse reflection spectra of BiYWO₆, Bi₂O₃, Y₂O₃, WO₃, Bi₂WO₆ and Y₂WO₆.

Fig. 6
Amounts of H₂ and O₂ produced on 0.5 wt% RuO₂-BYW under visible light irradiation.
Besides BYW, another novel visible-light-driven Bi$_x$Y$_{1-x}$VO$_4$ (BYV) solid solution in the tetragonal zircon type was synthesized by the solid-state reaction. The crystal structure of BYV was dependent on the $x$ value: it was a single phase solid solution oxides with tetragonal zircon type in $0 < x < 0.75$; however it was regarded as a mixture changing from tetragonal structure to monoclinic one in $0.75 < x < 1$. The tetragonal BYV ($0 < x < 0.75$) solid solution oxides loaded with Rh (1 wt%)-CuO (1 wt%) were discovered to split water to stoichiometric hydrogen and oxygen under visible light up to 510 nm. Among these catalysts, Bi$_{0.375}$Y$_{0.625}$VO$_4$ showed the best photocatalytic activity for overall water splitting in all the samples under either full arc or visible light irradiation (Fig. 8), of which the apparent quantum efficiency reached 0.72% at 420 nm light irradiation. BYV solid solution was proved to remain high photocatalytic activity as well as stable crystal structure and chemical states in the surface in the repeated runs. For tetragonal BYV ($0 < x < 0.75$) solid solution, Bi6s lone pair formed new valence band and increased the light absorption range to about 520 nm from the 420 nm of zircon-type BiVO$_4$ due to the distortion of Bi(Y)O$_8$ and VO$_4$ polyhedrons. The photocatalytic activity of BYV for overall water splitting might be attributed to the single zircon-type structure with distorted Bi(Y)O$_8$ dodecahedron and VO$_4$ tetrahedron as well as the cocatalyst providing active site.

In summary, I succeeded to develop visible-light-responding photocatalysts for overall water splitting by applying the band engineering technique by the formation of solid solutions. Although the quantum efficiency of the photocatalytic overall water splitting is still low, the steady progress in the material development will lead the usage of “solar hydrogen” in the future.

References


