Development of a New Photocatalytic Water Splitting System toward Solar Hydrogen Production

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Visible-light-driven water splitting systems

Water splitting system based on two-step photoexcitation

Visible light

$e^-$

$e^-$

$e^-$

$e^-$

$e^-$

$e^-$

$e^-$

$e^-$

$e^-$

Visible light

Red

Ox

H$_2$ evolution photocatalyst

SrTiO$_3$·Cr

TaON

BaTaO$_2$N

CaTaO$_2$N

Ta$_3$N$_5$

O$_2$ evolution photocatalyst

WO$_3$

TaON

CaTaO$_2$N

Organic dyes


Water splitting using efficient oxynitride electrodes

Utilization of solar light energy

Total energy emitted by the Sun
3.8 \times 10^{26} \text{ W}

Amount of energy reaching the surface of the Earth, ca. 8.5 \times 10^{16} \text{ W} = 85000 \text{ TW}

Solar energy available on the surface of the Earth ca. 1 \times 10^{15} \text{ W} = 1000 \text{ TW}

Total energy consumption by humankind (in 2004) ca. 1.3 \times 10^{13} \text{ W} = 13 \text{ TW}

Development of an efficient solar-light energy conversion system could be of tremendous help in meeting our future energy needs
Photocatalytic water splitting into $\text{H}_2$ and $\text{O}_2$

Potential application to the **direct production of $\text{H}_2$** for clean energy using abundant solar light

Various photocatalysts have been reported to have activity for water splitting into $\text{H}_2$ and $\text{O}_2$ **under UV light irradiation**
The utilization of visible light is clearly a key requirement for the practical use. However, water splitting under visible light has been quite difficult to achieve. The maximum solar energy conversion efficiency for water splitting ($\Delta G^\circ = 237$ kJ/mol) with 100% quantum efficiency is approximately 32%.
Why water splitting by visible light is difficult

There are few stable semiconductors having both a visible light absorption ability and a sufficient potential for water splitting.
Various visible light responsive photocatalyst can be applied in two-step system

**O₂ evolution**: Visible light responsive oxides (WO₃, BiVO₄)

**H₂ evolution**: Non-oxides (sulfides, oxynitrides, or organic dyes)
Visible light induced water splitting with two-step photoexcitation

**$\text{H}_2$ evolution photocatalyst**

**SrTiO$_3$(Cr-doped)**

**$\text{O}_2$ evolution photocatalyst**

**WO$_3$**

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**The world’s first demonstration** of visible light driven overall water splitting

Water splitting system using broader solar spectrum

\[ \text{Visible light} \rightarrow \text{H}_2 \text{ evolution photocatalyst} \]

\[ \text{Visible light} \rightarrow \text{O}_2 \text{ evolution photocatalyst} \]

- \( \text{WO}_3 \)
- \( \text{TaON} \)
- \( \text{SrTiO}_3/\text{Cr-doped} \)
- \( \text{TaON} \)
- \( \text{CaTaO}_2\text{N} \)
- \( \text{BaTaO}_2\text{N} \)

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Collaborative works with Prof. Domen
Overall water splitting using organic dyes

Time courses of H₂ and O₂ evolution using a mixture of NKX-2677 dye-adsorbed Pt/H₄Nb₆O₁₇ (50 mg) and IrO₂-Pt/WO₃ (100 mg) suspended in a 5 mM of KI aqueous solution under visible light.

First demonstration of overall water splitting using dyes as a photosensitizer

Summary

We have developed a new type of photocatalysis system that can split water into H$_2$ and O$_2$ under visible light irradiation, which was inspired by the two-step photoexcitation (Z-scheme) mechanism of natural photosynthesis in green plants.

The introduction of a Z-scheme mechanism reduces the energy required to drive each photocatalysis process, extending the usable wavelengths significantly (~660 nm for H$_2$ evolution and ~600 nm for O$_2$ evolution) from that in conventional water splitting systems (~460 nm).

Future tasks

Improvement of quantum efficiency (~7% at 420 nm) for practical application (at least ~30% at 600nm).

Construction of a system that can generate H$_2$ separately from O$_2$ to minimize the danger of explosions.
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