Wavelength-Tailored Photon-Assisted Catalysis: Optimizing Interfacial Dynamics for Solar Fuel Production

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Research Ideas Discussion with
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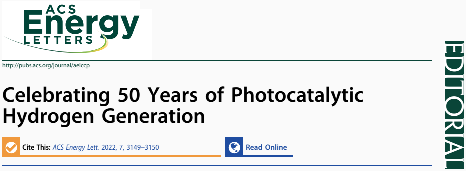
The University of Tokyo

January 23, 2025

Setting the Context



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Celebrating 50 Years of Photocatalytic Hydrogen Generation

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EDITORIAL

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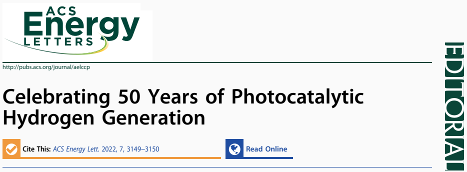

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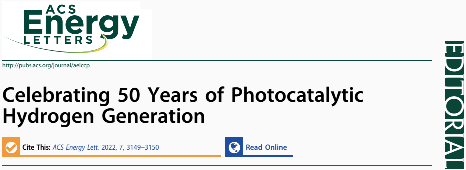

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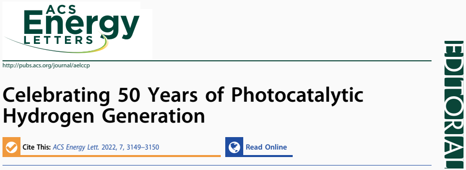
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- Computer-aided material discovery

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Need for a Paradigm Shift

Move from material-centric approaches towards comprehensive understanding of light-matter interactions in catalytic processes

Background: Light-Matter Interactions

Key Concepts

- Primary process: Charge carrier excitation under controlled light conditions
- Photon absorption follows exponential decay:

$$\text{Photon Intensity} \propto e^{-\alpha x}$$

- Penetration depth (skin depth):

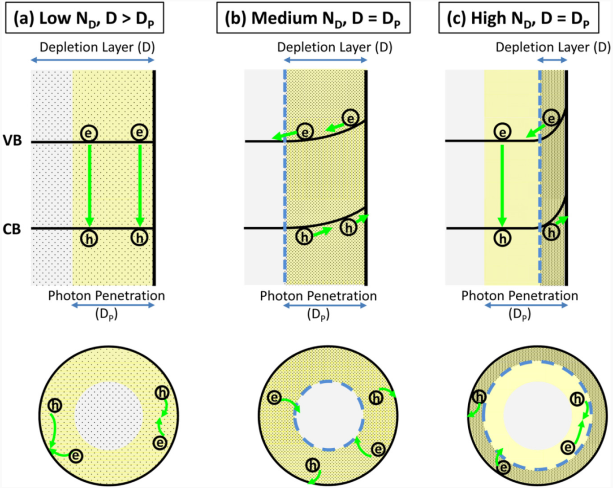
$$\delta = \frac{1}{\alpha} \text{ or } \alpha^{-1}$$

Material Examples

Penetration depth

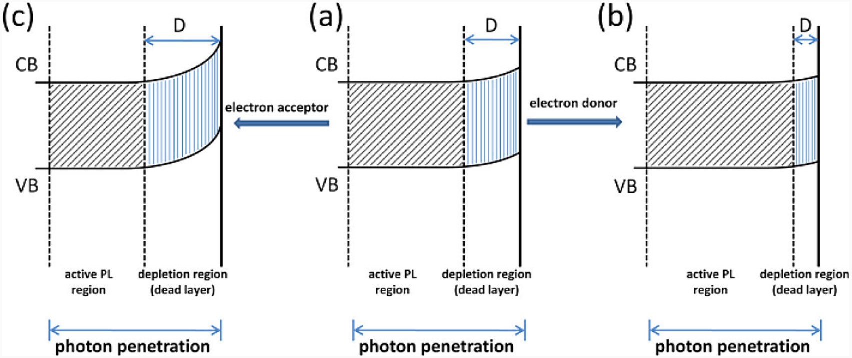
- Fe_2O_3: 118 nm (at 550 nm)
- CdTe: 106 nm (at 550 nm)
- Si: 680 nm (at 510 nm)

Dopant Concentration and Band Bending



Chemical Reviews, 2012, 112(10), 5520-5551

Surface Band Bending of TiO_2



Electron donor molecules (1-C_4H_8, C_3H_6, $C_2H_5C \equiv CH$, $CH_3C \equiv CH$, C_2H_4, $HC \equiv CH$, H_2O, H_2); electron acceptor molecules (O_2, N_2O)

Chem. Rev. 2012, **112**, 5520–5551; *Bull. Chem. Soc. Jpn.* 1991, **64**, 543; *J. Am. Chem. Soc.* 1988, **110**, 4914

Current Challenges in Photon Management

Current Practice

- Use of broad spectrum sources
  - AM1.5
  - Xe lamps
  - Hg lamps
- Focus only on bandgap excitation

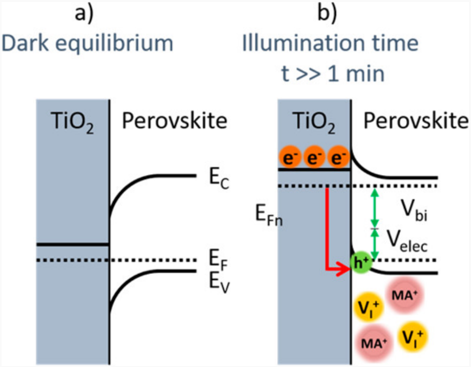
Resulting Issues

- Non-uniform penetration depths
- Variable charge carrier generation
- Increased recombination rates
- Poor control over excitation region

Important Consideration

Penetration depth should match space charge layer thickness

Pulsed Illumination



ACS Energy Lett. 2017, 2, 5, 950–956

- Short 1 s light pulse can change the interfacial dynamics, meaning that ions can somewhat rearrange themselves at the interface in that time scale.
- Enhances the interface stability

Impact of Material Modifications

Factors Affecting Space Charge Layer

1. **Doping**
    - Alters electrical properties
    - Modifies space-charge layer extent
2. **Metal Deposition**
    - Creates Schottky junctions
    - Influences charge separation
3. **Molecular Adsorbents**
    - Modify surface states
    - Affect band bending

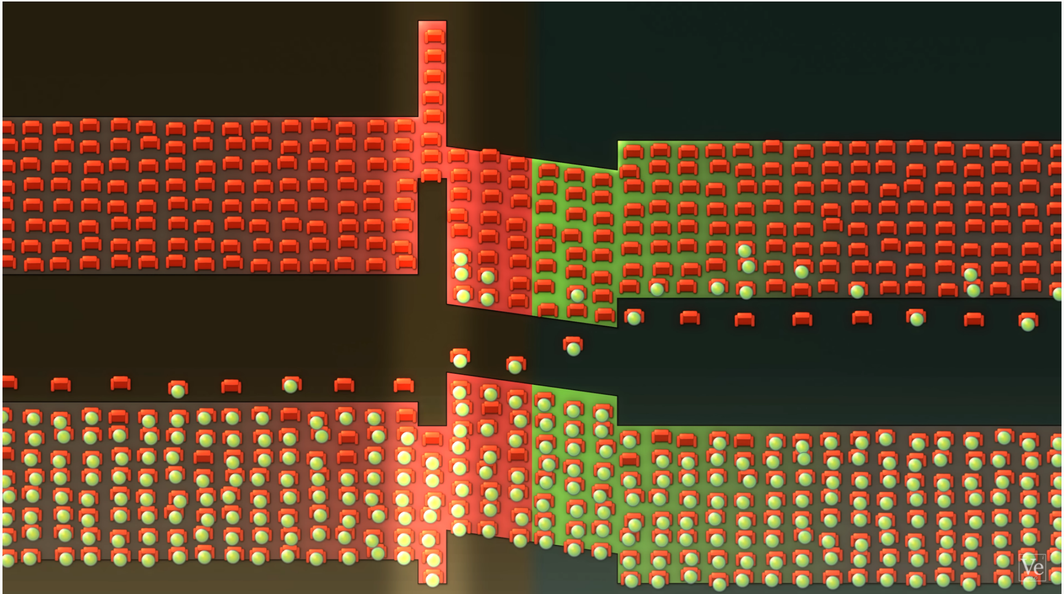
Iron Oxide Case
Iron Oxide Band Gap : 2.2 eV (564 nm)| Fe_2O_3: 118 nm (at 550 nm)

Key Insight
Monochromatic, tailored wavelength selection is crucial - not arbitrary choice

The Design of Photocatalyst: Current Paradigm

Current Approach	**Proposed Idea**
Bandgap, band edge matching	Match photon penetration with space charge layer
Broad spectrum light	Monochromatic, tailored wavelength, Intensity Optimization, Pulse Radiation
Static material design	Dynamic consideration of surface modifications
Overlooked surface changes	Consider adsorbate-induced band bending
Less attempt to prepare high quality defect less photoelectrode	MOCVD

Reversing Blue LED Mechanisms for Photoelectrocatalysis



Key Research Objectives

- **Material Optimization via MOCVD**: Utilize Metal-Organic Chemical Vapor Deposition (MOCVD) to modify and optimize heterostructures for photoelectrochemical water splitting, ensuring alignment between photon penetration depth and SCL thickness.
- **Band Structure and Interface Engineering**: Engineer the band structure and interfaces of wide bandgap semiconductors to enhance charge separation efficiency, minimizing electron-hole recombination.
- **Surface Modifications and Co-Catalyst Development**: Develop and apply surface treatments and integrate co-catalysts to facilitate efficient water splitting reactions, ensuring compatibility with holistic light management strategies.

Innovative Approach: Holistic Photon Management

The approach emphasizes the critical alignment of photon penetration depth with the SCL, ensuring that electron-hole pairs are generated within the region where internal electric fields can effectively separate them. This involves:

- **Wavelength Tailoring**: Selecting specific wavelengths to match the absorption coefficient and penetration depth with the SCL thickness, optimizing spatial charge separation.
- **Intensity Optimization**: Balancing light intensity to generate sufficient charge carriers without inducing band flattening, thereby maintaining effective charge separation.
- **Temporal Control**: Implementing pulsed illumination to mitigate photocatalyst degradation and manage carrier dynamics, enhancing both efficiency and longevity.

Moving Forward

Thank You for Your Time and Attention

Your insightful questions and comments have been invaluable.

I welcome any suggestions or opinions you may have to further improve this research proposal.