The Future of Photon-Assisted Catalysis

Do We Require a Paradigm Shift?

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Statement of Problem

- **Limited Understanding**: Complex interplay between material properties, light characteristics, and catalytic performance
- **Traditional Focus**: Emphasis on material modification while overlooking crucial role of wavelength and intensity of incident photons
- **Systematic Studies**: Lack of comprehensive research on photon characteristics-catalytic performance relationship
- **Methodology Gaps**: Fragmented efforts and absence of standardized experimental protocols

Need for Paradigm Shift

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

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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):

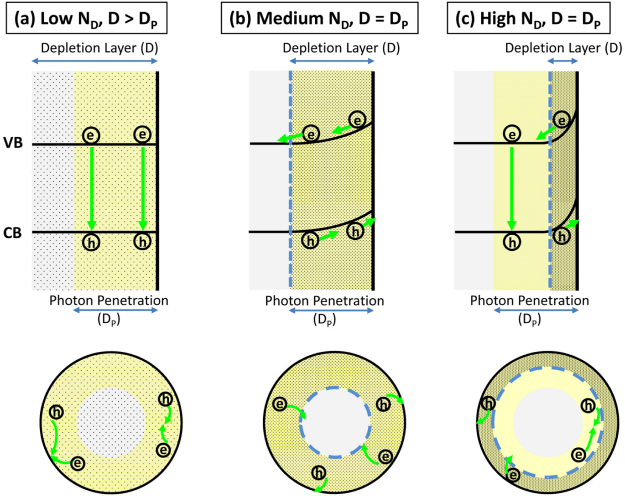
$$\delta = \frac{1}{\alpha} \text{ or } \alpha^{-1}$$

Material Examples

Penetration depth

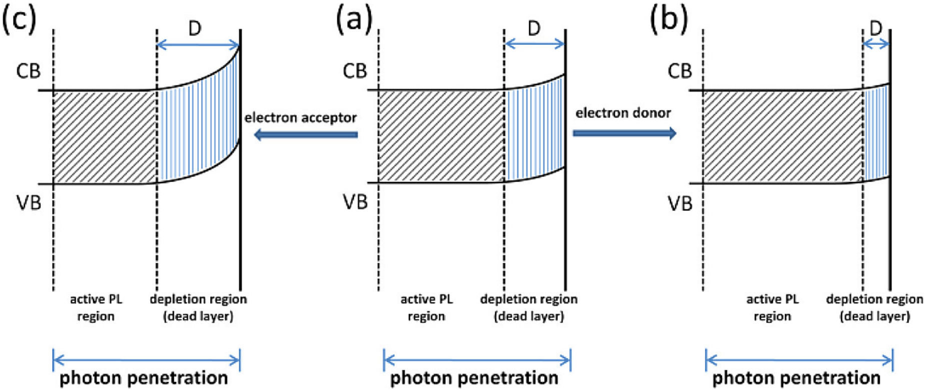
- Fe_2O_3: 118 nm (at 550 nm)
- CdTe: 106 nm (at 550 nm)
- Si: 680 nm (at 510 nm)

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

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

Key Insight

Monochromatic, tailored wavelength selection is crucial - not arbitrary choice

The Design of Photocatalyst: Current Paradigm

Current Approach	Proposed Idea
Bandgap matching only	Match photon penetration with space charge layer
Broad spectrum light	Monochromatic, tailored wavelength
Static material design	Dynamic consideration of surface modifications
Overlooked surface changes	Consider adsorbate-induced band bending

Proposed paradigm shift based on recent experimental observations

Photothermal Conditions

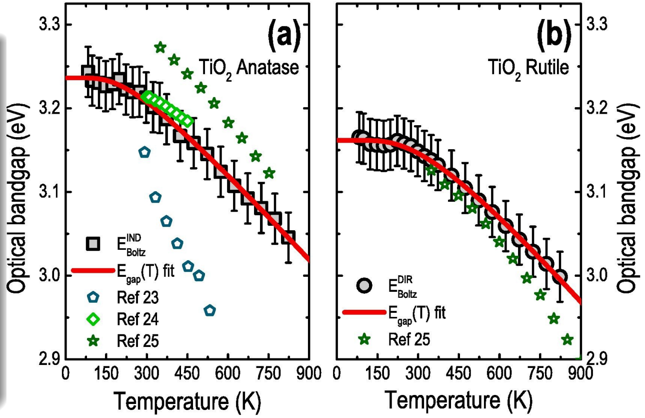
Temperature Dependent Bandgap, Varshni Equation

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (1)$$

where:

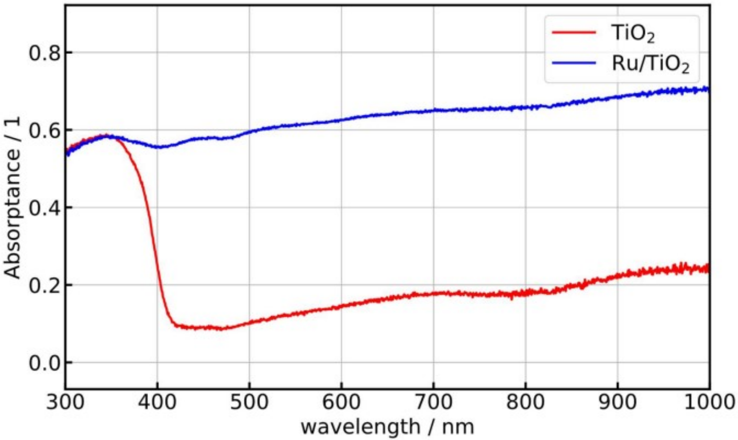
- $E_g(T)$: Bandgap at temp. T
- $E_g(0)$: Bandgap at 0K
- α, β: Material constants

Physica, **34**(1), 1967, 149-154

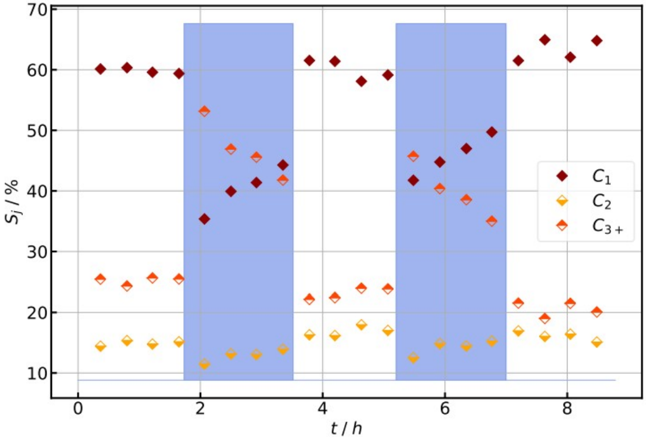


Results in Physics, 60, 2024, 107653

Photothermal Conditions



ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-606hv

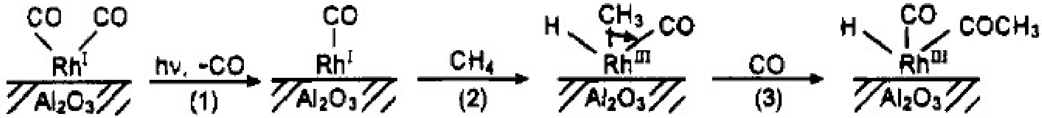


ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-606hv

Key Inferences

- Methane selectivity increases over time
- $C_3{}^+$ selectivity decreases over time
- Chances of Reverse Oxidation
  - Photo-oxidation of hydrocarbons over Ru/TiO_2

Methane Photo-Activation



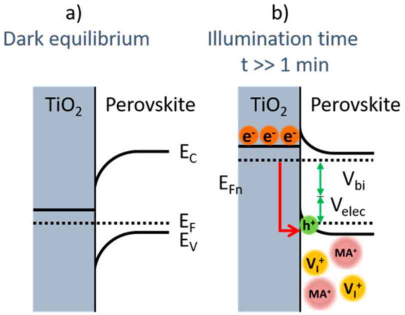
(1): Photodecomposition of rhodium dicarbonyl to form a 16-electron intermediate.

(2): Oxidative addition of the monocarbonyl intermediate to the C-H bond of methane.

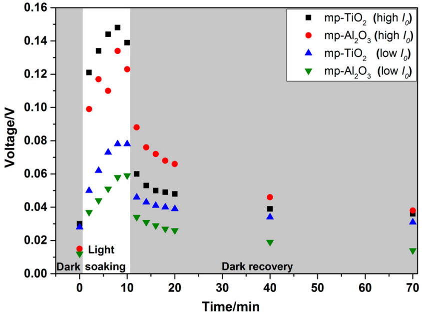
(3): Migratory-insertion of CH_3 to form a proposed acetyl ligand; subsequently an additional CO fills the vacant Rh site.

J. Phys. Chem. 1995, 99, 12640-12646

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



ACS Energy Lett. 2017, 2, 5, 950–956



ACS Energy Lett. 2017, 2, 5, 950–956

Plausible Recommendation

1. Selection of wavelength and intensity of light to be irradiated is not arbitrary but tailored with materials and modifications
2. A detailed study of photosorption is required to elucidate the exact mechanism
3. The optical charactarization of the catalyst should be characterized at the photothermal reaction conditions
4. Wide band gap is preferred because of the stability and control of the material properties.
5. Defining Photothermal, Photocatalytic or Photosynthetic, Photon-assisted Process

Thank You!

1. T. Wolkenstein (1991). Electronic Processes on Semiconductor Surfaces During Chemisorption. Netherlands: Springer US.
    - Chapter 7 The Effect of Illumination on the Adsorptive and Catalytic Properties of a Semiconductor.
    - Chapter 8 Adsorption and Luminescence.
2. Bube, R. H. (1960). Photoconductivity of Solids. United States: Wiley.
3. John T Yates Works