

### UNIT 3: INORGANIC PHOTOCHEMISTRY (9 HRS)

3.1 Excited states in transition metal complexes: Intra-ligand excited states and metal centred excited states. Photochemical reactions: Substitution and redox reactions of Cr(III), Co(III), Rh(III) and Ru(II) complexes, manganese-based photosystems for the conversion of water into oxygen, applications-synthesis and catalysis, chemical actinometry and photochromism, metal-metal multiple bonds, dissociative photochemistry, ligand loss.

3.2 Metal complex sensitizers, electron relay, semiconductor supported metal oxide systems, water photolysis, nitrogen fixation and CO<sub>2</sub> reduction, dinitrogen splitting.

#### PART 2

### MANGANESE-BASED PHOTOSYSTEMS FOR THE CONVERSION OF WATER INTO OXYGEN

Manganese (Mn) sparks the photosynthesis process by splitting water after Photosystem II (PSII) fixes light to initiate the conversion of CO<sub>2</sub> and water into carbohydrates.



The water-oxidizing complex (WOC), also known as the oxygen-evolving complex (OEC), of photosystem II in oxygenic photosynthetic organisms efficiently catalyzes water oxidation. *Pirson* was the first to discover that Mn is essential for oxygenic photosynthesis and extensive research since then has led to the establishment of the PSII pigment-protein complex to be responsible for photosynthetic oxygen evolution. Manganese-based catalytic systems including Mn-terpy dimer/titanium oxide, Mn-oxo tetramer/Nafion, Mn-terpy oligomer/tungsten oxide, manganese-calcium (Mn<sub>4</sub>CaO<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub>) cluster which are highly active in water oxidation catalysis.

Water oxidation to produce one oxygen molecule requires the removal of four electrons, and Kok et al proposed an explanation for the observed oscillation of the oxygen evolution pattern. Kok's hypothesis was that in a cycle of water oxidation, a succession of oxidizing equivalents is stored at the WOC, and when four oxidizing equivalents have accumulated one by one, an

# Inorganic Photochemistry Lecture Notes

**RD Boyd**



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## **Table of Contents Inorganic Photochemistry Lecture Notes**

1. Understanding the eBook Inorganic Photochemistry Lecture Notes
  - The Rise of Digital Reading Inorganic Photochemistry Lecture Notes
  - Advantages of eBooks Over Traditional Books
2. Identifying Inorganic Photochemistry Lecture Notes
  - Exploring Different Genres
  - Considering Fiction vs. Non-Fiction
  - Determining Your Reading Goals
3. Choosing the Right eBook Platform
  - Popular eBook Platforms
  - Features to Look for in an Inorganic Photochemistry Lecture Notes
  - User-Friendly Interface
4. Exploring eBook Recommendations from Inorganic Photochemistry Lecture Notes

- Personalized Recommendations
  - Inorganic Photochemistry Lecture Notes User Reviews and Ratings
  - Inorganic Photochemistry Lecture Notes and Bestseller Lists
5. Accessing Inorganic Photochemistry Lecture Notes Free and Paid eBooks
    - Inorganic Photochemistry Lecture Notes Public Domain eBooks
    - Inorganic Photochemistry Lecture Notes eBook Subscription Services
    - Inorganic Photochemistry Lecture Notes Budget-Friendly Options
  6. Navigating Inorganic Photochemistry Lecture Notes eBook Formats
    - ePub, PDF, MOBI, and More
    - Inorganic Photochemistry Lecture Notes Compatibility with Devices
    - Inorganic Photochemistry Lecture Notes Enhanced eBook Features
  7. Enhancing Your Reading Experience
    - Adjustable Fonts and Text Sizes of Inorganic Photochemistry Lecture Notes
    - Highlighting and Note-Taking Inorganic Photochemistry Lecture Notes
    - Interactive Elements Inorganic Photochemistry Lecture Notes
  8. Staying Engaged with Inorganic Photochemistry Lecture Notes
    - Joining Online Reading Communities
    - Participating in Virtual Book Clubs
    - Following Authors and Publishers Inorganic Photochemistry Lecture Notes
  9. Balancing eBooks and Physical Books Inorganic Photochemistry Lecture Notes
    - Benefits of a Digital Library
    - Creating a Diverse Reading Collection Inorganic Photochemistry Lecture Notes
  10. Overcoming Reading Challenges
    - Dealing with Digital Eye Strain
    - Minimizing Distractions
    - Managing Screen Time
  11. Cultivating a Reading Routine Inorganic Photochemistry Lecture Notes
    - Setting Reading Goals Inorganic Photochemistry Lecture Notes
    - Carving Out Dedicated Reading Time
  12. Sourcing Reliable Information of Inorganic Photochemistry Lecture Notes

- Fact-Checking eBook Content of Inorganic Photochemistry Lecture Notes
  - Distinguishing Credible Sources
13. Promoting Lifelong Learning
- Utilizing eBooks for Skill Development
  - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
  - Interactive and Gamified eBooks

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