

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 CO₂ 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 CO₂ 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 (Mn₄CaO₅(H₂O)₄) 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

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