
Synopsis

Thesis Title: Rational Design of Cadmium Sulfide based Nano-hybrid Materials: Synthesis, Characterization and Evaluation of Photocatalytic Properties for Efficient Hydrogen Generation and Organic Dye Degradation

Name of the Student: Ziyauddin Khan

Roll Number: 08612211

Department: Chemistry

Thesis Supervisor: Dr. Mohammad Qureshi

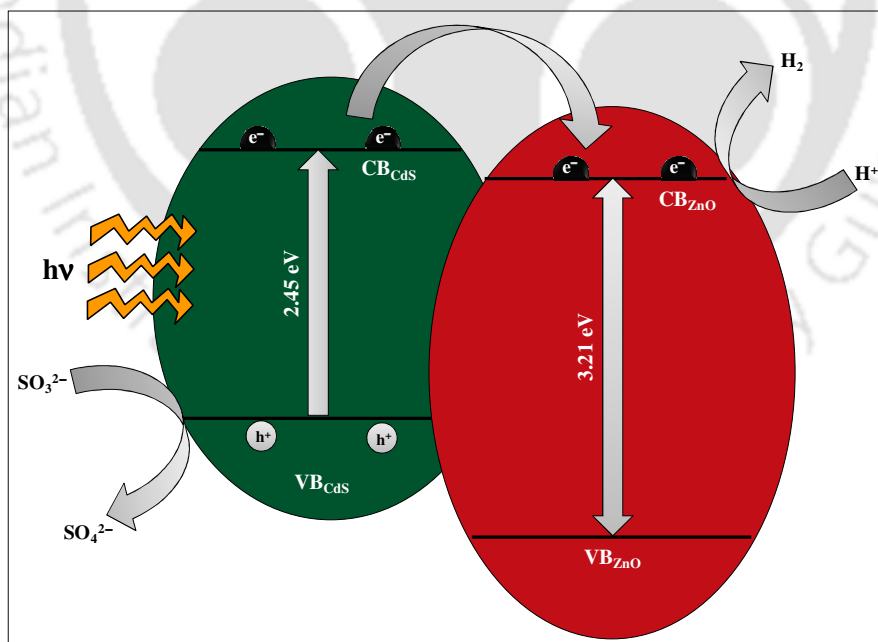
Degree for which submitted: Doctor of Philosophy

Chapter 1 presents the basic concepts and literature survey of the photocatalytic water splitting. Brief overviews on the synthesis of efficient photocatalytic materials for hydrogen generation as well as for dye degradation by the different methodologies are discussed.

Chapter 2 presents the detailed synthesis of CdS based hybrid photocatalysts and their characterization. Special interest is given to the description of in-house built photocatalytic measurement set-up along with the gas chromatographic (GC) instrumentation. This chapter also demonstrates the detailed experimental procedure for hydrogen generation and organic dye degradation. We have explained the method for the calculation of apparent quantum yield for hydrogen generation. A brief description of the freeze-thaw cycle performed for the mechanistic (for the presence of intermediate, such as superoxide radical) study of dye degradation is also discussed.

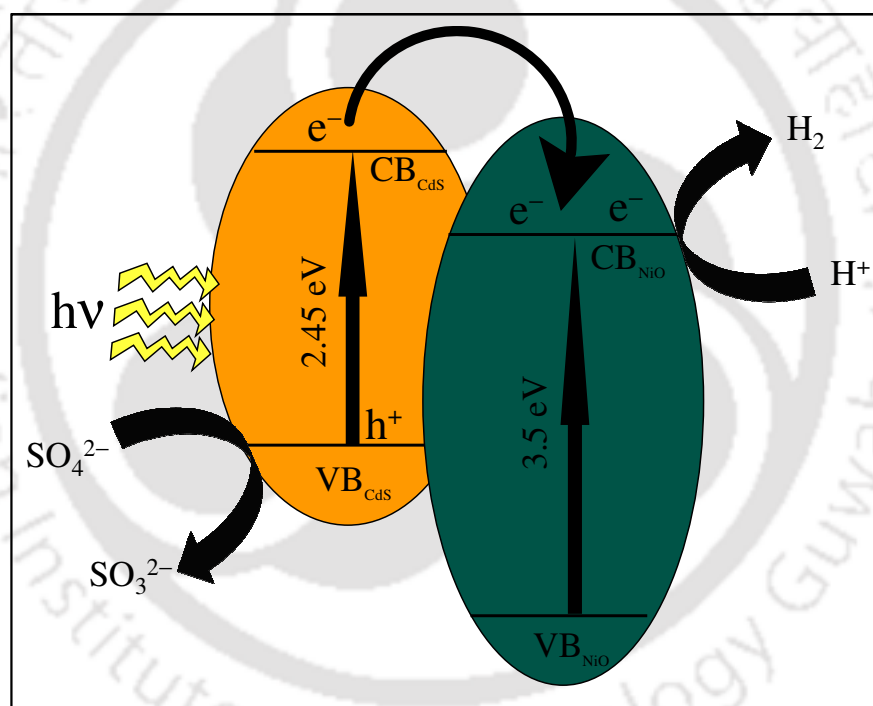
Chapter 3 Divided in two parts:

Chapter 3A presents the results of the investigations due to the enhanced specific surface area and the coupling effect of Al_2O_3 and ZnO wide band gap materials with that of CdS on photocatalytic activity. 3D $\text{Al}_2\text{O}_3/\text{CdS}$ and ZnO/CdS exhibits enhanced photocatalytic activity for hydrogen generation with apparent quantum yields (AQY) of 11% and 15% respectively. The high hydrogen production rate of ZnO/CdS is mainly attributed to the enhanced surface area and the facile charge transfer between CdS and ZnO (scheme 1). 3D $\text{Al}_2\text{O}_3/\text{CdS}$ and ZnO/CdS show highly efficient dye degradation in comparison to that of 1D CdS NWs. The kinetic study of methyl orange degradation is carried out and found to follow first order kinetics with apparent rate constant 0.032 min^{-1} for 3D $\text{Al}_2\text{O}_3/\text{CdS}$ and 0.053 min^{-1} for 3D ZnO/CdS. The evidence for the formation of superoxide radical anion ($\text{O}_2^{\cdot-}$) and hydroxyl radical ($\cdot\text{OH}$) were performed using freeze-thaw cycle.



Scheme 1 Schematic illustration of the efficient electron transfer and the band energy positions of ZnO and CdS in the hierarchical 3D ZnO/CdS binary heteroarrays

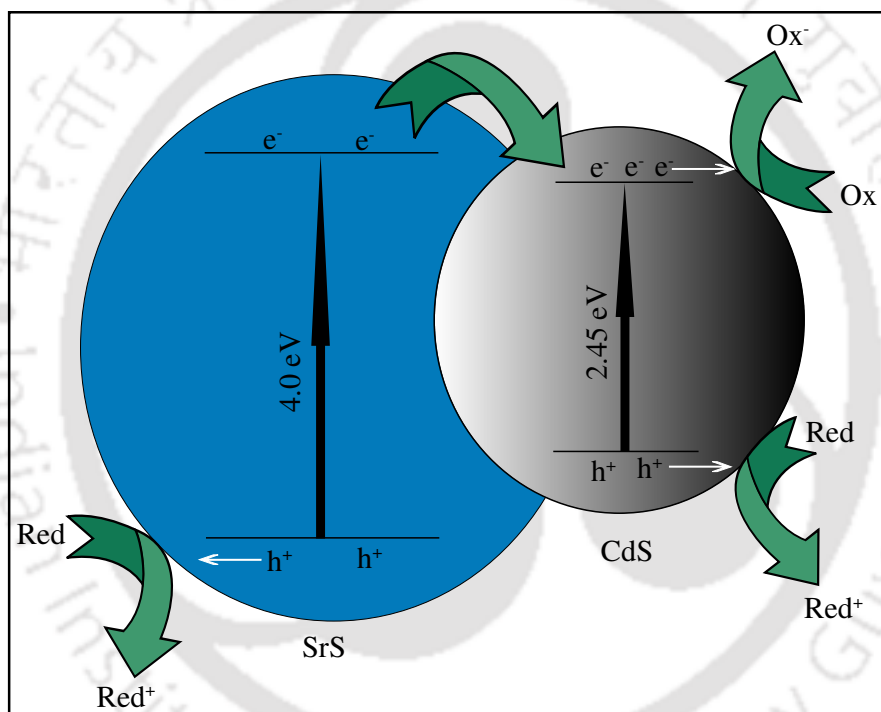
Chapter 3B describes the effect of enhanced specific surface area and facile charge transfer on the photocatalytic activity. As prepared 3D NiO/CdS show high efficiency for photocatalytic hydrogen generation with an apparent quantum yield (AQY) of 6% in comparison to that of 1D CdS nanowires (NWs) and bulk CdS under visible light irradiation. The enhanced hydrogen production rate in 3D NiO/CdS is attributed to the high specific surface area and facile charge transfer from conduction band (CB) of CdS to CB of NiO due to the favorable energy alignments of CB of CdS and CB of NiO (scheme 2).



Scheme 2 Schematic illustration of the efficient electron transfer and the band energy positions of NiO and CdS in the hierarchical 3D NiO/CdS binary heteroarchitecture, under visible light irradiation

Chapter 4 describes the effect of enhanced specific surface area and facile charge transfer on photocatalytic activity under UV-Vis irradiation. As synthesized hierarchical 3D SrS/CdS show high efficiency for hydrogen generation with an apparent quantum yield

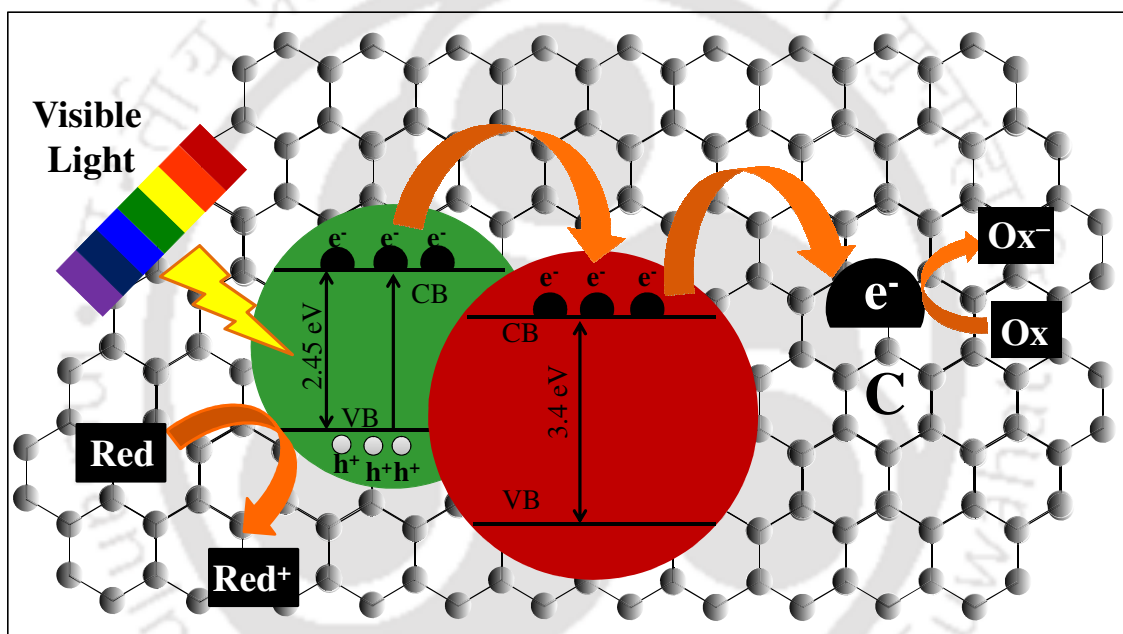
(AQY) of 10% and ~ 100% methyl orange dye degradation in comparison with 1D CdS NWs, SrS nanoparticles and bulk CdS under UV-Visible light irradiation. The enhanced photocatalytic activity of 3D SrS/CdS is attributed to high specific surface area and facile charge transfer from CB of SrS to CB of CdS due to the favorable energy alignments of CB of SrS and CB of CdS (scheme 3). Mechanistic study of dye degradation involving the intermediates such as superoxide radical anion ($O_2^{\cdot-}$) and hydroxyl radical ($\cdot OH$) were explained.



Scheme 3 Schematic presentation of efficient charge transfer, band position of SrS and CdS in hierarchical 3D SrS/CdS heteroarrays under UV-Vis light irradiation

Chapter 5: In this chapter we have demonstrated a single step hydrothermal synthesis of CdS/Metal Oxide (MO = ZnO, Al_2O_3) and examine their photocatalytic activity in presence of graphene oxide. CdS/ Al_2O_3 /GO and CdS/ZnO/GO both exhibits enhanced photocatalytic activity for hydrogen generation with apparent quantum yields (AQY) of

14% and 30% respectively. Moreover, CdS/MO/GO displayed efficient photodegradation of organic dye; ~ 90% for CdS/Al₂O₃/GO and ~99% for CdS/ZnO/GO. The high photocatalytic activity of CdS/MO/GO is attributed to the presence of graphene oxide which provides large surface area for effective mass transfer and facile charge transfer that reduces the recombination rate of photoinduced charge carriers (scheme 4). The present study highlights the potential application of graphene based materials in the field of energy conversion and environment remediation.



Scheme 4 Schematic presentation of efficient charge transfer, band position and redox processes involve in CdS/ZnO/GO under visible light irradiation