

Particulate models in heterogeneous photocatalysis

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Heterogeneous photocatalysis provides means to produce fuels/chemicals at the expense of solar energy. The development and application aspects of various semiconductor particulate models in heterogeneous photocatalysis constituted primarily the common aim of achieving efficient charge separation. In this article, the electron and energy transfer processes associated with these particulate models have been discussed and the experimental performance of the systems constructed based upon these models have been contrasted in the light of the more efficient and simpler systems. The potential of the semiconductor catalysts for water decomposition, hydrogen evolution from H_2S /sulphidic media, fixation of nitrogen and carbondioxide reduction has been highlighted. The entry of nanosize semiconductor photocatalysts in heterogeneous photocatalysis has been addressed. The important areas of applications of photocatalysis in organic synthesis, pollution treatment, area-selective reactions to generate light images and metallic patterns have also been incorporated in this review.

PHOTOCATALYSIS is a direct quantum conversion process and as in the case of photovoltaics, photoelectrochemistry and photosynthesis, it has been investigated for utilizing solar energy to produce value-added chemicals. Substantial progress has been made in the field of photocatalysis in the bench scale. In order to achieve applications with high efficiency and economy it is realized that lot more work has to be done before any commercially viable system can be developed. While reviewing the literature it is recognized that in the period immediately after 1970's more emphasis was given to the development of an 'apparatus' that produces electrical/fuel energy efficiently; however, since the end of 1980's the emphasis seemed to have been towards the understanding of basic processes involved in 'light-harvesting systems'. While water-splitting process is extensively studied, photofixation of nitrogen, photoreduction of carbondioxide, photocatalytic destruction of pollutants, recovery of trace metals etc., have also received considerable attention. Photocatalysis has been investigated for various applications and has been the subject of several international conferences¹⁻⁴. A few review articles⁵⁻⁸

have appeared bringing out the fundamental aspects related to photocatalysis. Recently, Fox and Dulay⁹ have reviewed the heterogeneous photocatalysis emphasizing its application in organic chemistry and also discussed experiments that elucidate mechanism of photocatalysis. In this article we attempt to give an overview of the subject emphasizing typical cases and giving examples from the studies carried out in our laboratories.

Role of semiconductor particles in photocatalysis

Water-splitting, photofixation of nitrogen, photoreduction of carbon dioxide and many other reactions do not occur on illumination with light alone. These reactions often require the use of Photocatalysts – a term that implies photon-assisted generation of catalytically – active species. The role of photons (sunlight in general) is to generate catalysts (excited states in the case of molecular photocatalysts, also called as sensitizers) or electron (e^-) – hole (h^+) pairs in the case of semiconductor materials that yield fuels or chemicals in subsequent dark (thermal) reactions.

Organic dyes, polypyridyl complexes, and metalloporphyrins in homogeneous media have been used as 'photosensitizers' to induce photoredox reactions. However in homogeneous solutions the major disadvantage is the energy-wasting back-electron transfer reaction to give back the starting material. To overcome this problem, studies on organized assemblies (micelles, vesicles, microemulsions etc.) as a means to mitigate back electron transfer have been undertaken by investigators working in this area. Heterogeneous semiconductor particulate/colloidal systems which act as light absorbing units offer an excellent route to overcome this problem. However, in this case too, strong $e^- - h^+$ recombination process is a formidable obstacle for realizing high efficiency in the photocatalytic processes. The development of effective means to suppress back-electron transfer or $e^- - h^+$ recombination process is vital for increasing chemical conversion efficiency. Various other reasons that justify the use of semiconductor particulates/colloids are (i) they are relatively inexpensive (ii) they have high

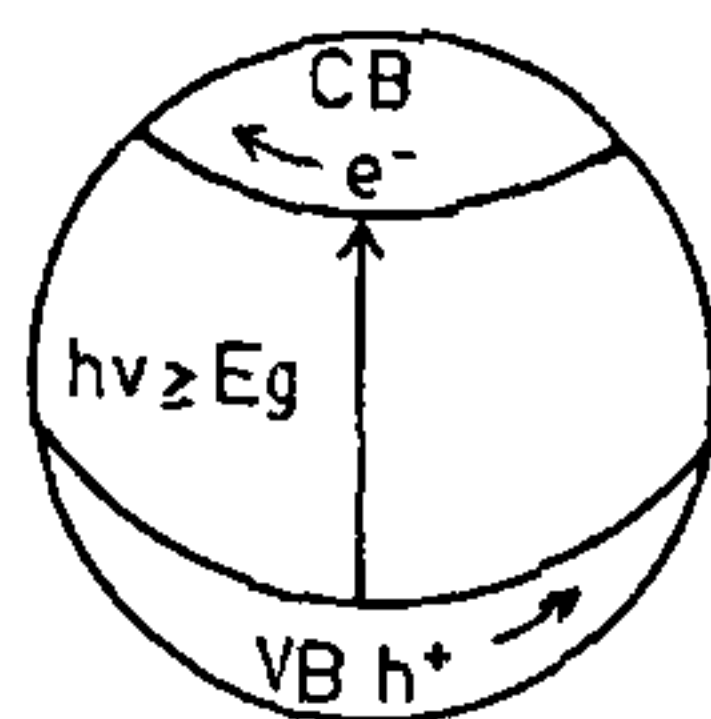


Figure 1. Hypothesized illuminated semiconductor particle $e^- - h^+$ pair formation.

surface area (iii) broad absorption spectra with high absorption coefficients (iv) their properties can be modified by size reduction (quantum size effects), derivatizations, doping, junction formations etc. (v) facility for multielectron transfer process and (vi) when desired, they may be used directly for driving some half reactions e.g. hydrogen evolution. In addition in semiconductor particle (exception, quantum size particles) like in bulk semiconductor, irradiation with light of energy equal to or greater than band-gap energy (E_g) leads to generation of pairs of $e^- - h^+$ by promotion of electrons from valence band (VB) to the conduction band (CB) (Figure 1). The $e^- - h^+$ generated thus can be used to drive chemical reactions provided: (a) the energy separation (band-gap) between e^- and h^+ is larger than the energy required for the desired reaction; (b) the redox potentials of the e^- and h^+ (thus the positions of CB and VB) are suitable for inducing redox processes and (c) the rates of these redox reactions are faster than or at least fast enough to compete with the electron-hole recombination. Therefore, development of efficient redox catalysts capable of making product formation competitive with these recombination processes is recognized to be important in this field. As will be seen later in this review, several investigators approached this problem in various discrete ways: by adapting semiconductor material modification (doping, depositing islands of metals/metal oxides, microheterojunctions between high and low-band gap materials, microemulsions, vesicle supporting, encapsulations, immobilizations etc.) or by changing the chemistry of the surrounding medium (pH, addition of promoters, sensitizers, electron relays, sacrificial electron donors etc.) we can make the product formation to outdo the recombination reaction.

Photocatalytic reactions

It is known¹⁰ that illumination together with application of small bias voltage to the single crystal TiO_2 electrode causes evolution of H_2 and O_2 simultaneously. This discovery acted as a nucleus for the enormous interest

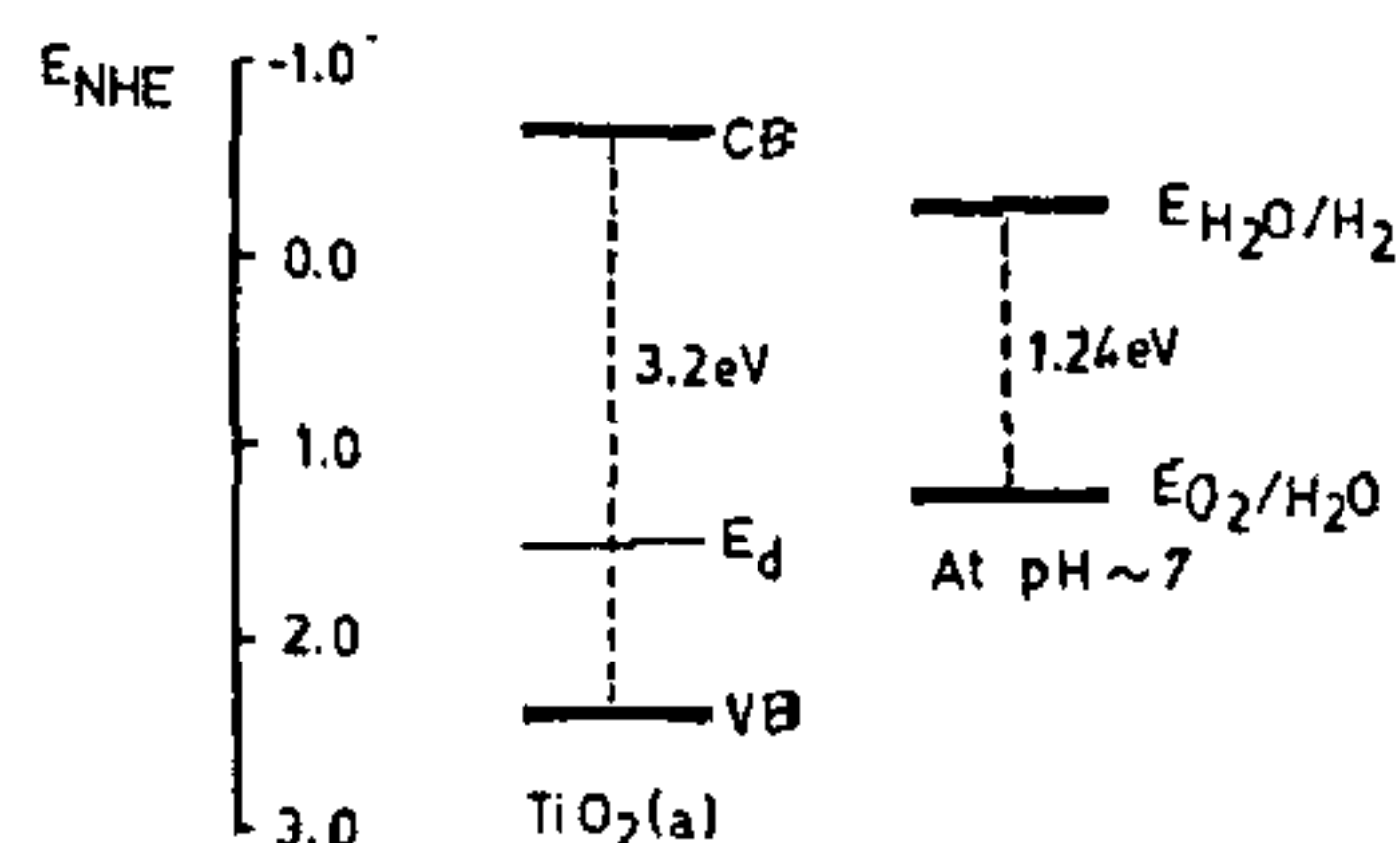


Figure 2. Simplified energy level diagram showing relative positions of valence and conduction bands in TiO_2 (anatase) semiconductor and hydrogen and oxygen redox couples in water.

developed subsequently in heterogeneous photocatalysis. A great deal of information has been accumulated on the photocatalytic water-splitting process over various oxidic, mixed oxidic non-oxidic chalcogenide type of semiconductors primarily with the aim of creating artificial water-splitting systems.

Using the energy diagram shown in Figure 2, it would be easy to understand the water-splitting process on TiO_2 semiconductor. Combining the facts that (i) the band edges of TiO_2 envelop the water reduction and water oxidation couples and (ii) the anodic decomposition potential of $\text{TiO}_2(E_d)$ is placed at more positive potential than the water oxidation couple itself, we understand that irradiation of TiO_2 semiconductor should lead to evolution of H_2 and O_2 in stoichiometric quantities. This conceptually simple cyclic water-splitting scheme has not been practically realized even today. This led to the adaption of various strategies wherein either semiconductor (surface or bulk) or aqueous medium is modified suitably. Thus, we find at least four light harvesting units for water-splitting processes, each one of them incorporating the idea of making redox processes faster than $e^- - h^+$ recombination process (see Figure 3a-d). On the other hand considerable progress has been made to optimize the half-cycles of water-splitting process independently. System a (Figure 3) exemplifies the use of sensitizer-electron relay components in conjunction with catalysts such as metal or metal oxide colloids. System b is a widely used metal (e.g. Pt) and metal oxide (e.g. RuO_2) deposited semiconductor particulate unit. System c is designed to avoid band-gap illumination (especially desirable with large band gap materials) by using visible light excitable sensitizer molecule. In system d the principle of interparticle electron transfer is introduced as a means to effectively separate e^- and h^+ . The presence of metals or metal oxides in general and Pt and RuO_2 in particular indeed helps the reactions (1) and (2) to compete with the recombination process of



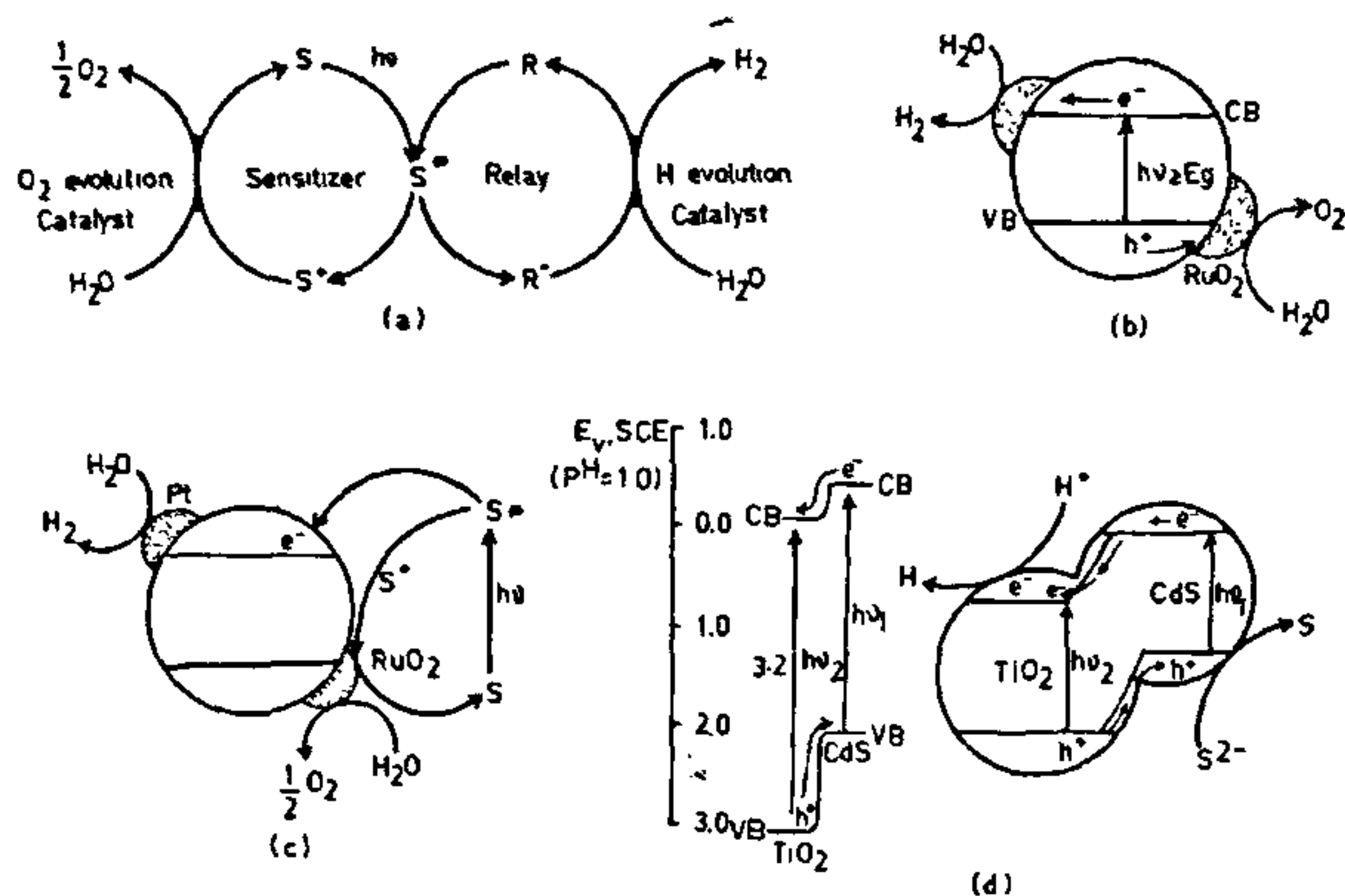
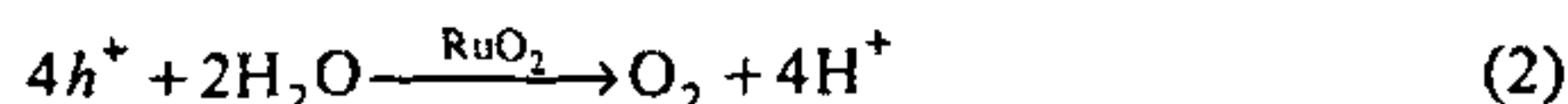


Figure 3. *a*, Metal(metal oxide)-sensitizer-relay water splitting system. *b*, A typical bifunctional redox catalysts supported over semiconductor particles. Light of energy equal to or greater than E_g needs to be used. *c*, Photosensitization of wide band gap semiconductor particulate system using a sensitizer (S) that has excitation maximum in the visible region and the electrons from the excited molecules (S^*) are pumped into conduction band of wide band gap semiconductor. *d*, A model representing the use of micro-heterojunction formation for efficient H_2 evolution from sulfidic media (high efficiency). Electrons are transferred into CB of the wide band gap semiconductor and holes are transferred into VB of the narrow band gap semiconductor and thus the electrons and holes are effectively separated in the heterojunction field.



e^-h^+ pairs generated by illumination². The idea of depositing metals as catalysts for H_2 evolution seems to have been borrowed from electrochemistry wherein their ability to lower overpotentials for water electrolysis is well known. Based on these four models discussed above considerable information is gathered for the feasibility of cyclic water cleavage, although the efficiencies of gas evolutions are rather low.

The photolysis of chemisorbed water on TiO_2 ^{11,12}, Pt/TiO_2 ^{13,14}, $SrTiO_3$ ^{15,16}, $M/SrTiO_3$ ¹⁷ ($M = Rh, Ru, Re, Ir, Pt, Pd, Os, \text{ and } Co$), mixed powders of TiO_2 and RuO_2 ¹⁸ and n/p type TiO_2/GaP particles¹⁹ has been reported.

Photocatalytic systems which can evolve H_2 and O_2 using sensitizer $[Ru(bpy)_3^{2+}]$ -relay $[MV]^{2+}$, and sacrificial electron donor $[EDTA]$ in conjunction with metal colloids²⁰, Pt/TiO_2 ²¹, Pt and RuO_2 ²², and $Pt/TiO_2/RuO_2$ ²³ have been studied for water decomposition. The photochemistry of polypyridine and porphyrin complexes has been recently reviewed by Kalyanasundaram²⁴. Our studies on Pt/TiO_2 , $Ru(bpy)_3^{2+}$, ascorbic acid system have shown that hydrogen evolution is facilitated by quick reduction of $Ru(bpy)_3^{3+}$ by ascorbic acid²⁵. A number of publications have reported the promoting effect of certain cations (doped TiO_2) or some anions in aqueous medium on the photocatalysis. Thus addition of Nb, Mg, Li and Ba^{2+} cations to TiO_2 dispersions under irradiation shows remarkable promoting effect²⁶. Further

an interesting effect of carbonate addition to water has been reported which significantly improved H_2 and O_2 yields²⁷ over Pt/TiO_2 . Sodium hexatitanate ($Na_2Ti_6O_{13}$) and barium tetratitanate ($BaTi_4O_9$) with incorporated RuO_2 ²⁸, ion-exchangeable potassium niobates²⁹⁻³⁰ ($K_4Nb_6O_{17}$) have been shown to exhibit stable photocatalytic activity for the stoichiometric production of H_2 and O_2 from water.

Another well-characterized semiconductor believed to be more suitable for the direct splitting of H_2O is cadmium sulphide³². Hydrogen production from CdS itself has been observed by several authors³³. The catalytic effect of Pt and RuO_2 has been exploited to stabilize small band-gap semiconductor particles, especially CdS . Sustained water cleavage by visible light has been reported with $Pt/CdS/RuO_2$ powder³⁴. Similarly, aqueous dispersions of CdS loaded with noble metal oxides³⁵ are shown to be capable of evolving O_2 upon illumination with visible light in the presence of $PtCl_6^{2-}$ as scavenger for CB electrons. Vesicle-stabilized, Rh -coated CdS ³⁶ has been found to generate hydrogen. The photocatalytic H_2 and O_2 generation has been reported from our laboratory using a CdS dispersion (CdS loaded with Pt, Ir, Rh and RuO_2) and a (μ -peroxo) $Ru(IV)$ -dioxygen complex as an electron relay³⁷. Use of the said relay molecule helps to catalyse the hole-mediated oxidation of OH^- to generate O_2 via the participation of superoxocomplex (see Figure 4).

Highest rates of hydrogen evolution have been reported³⁸ with zinc sulphide catalyst in aqueous media.

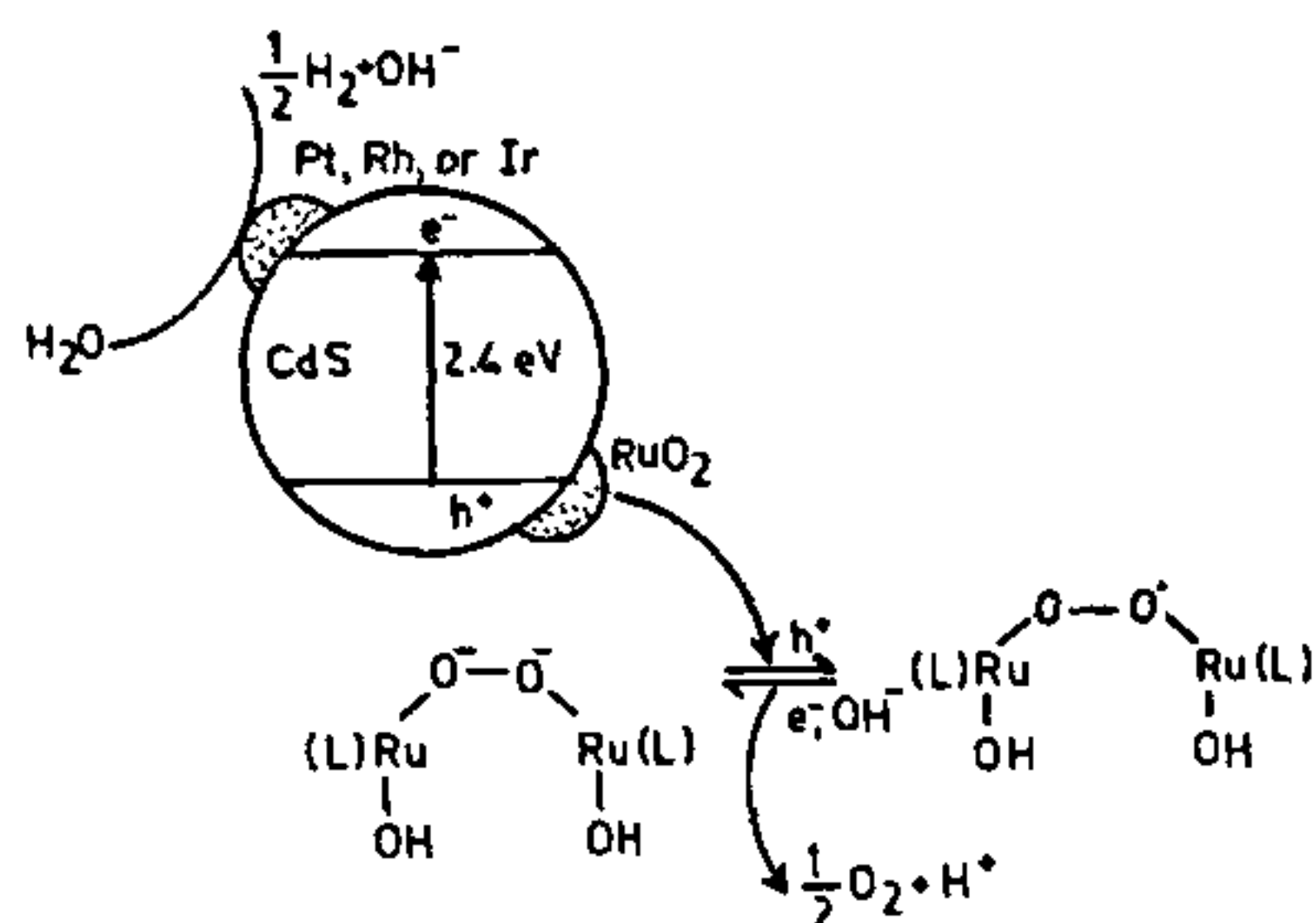


Figure 4. A model particulate system elucidating the use of bifunctional redox catalyst (Pt, Rh, or Ir)/CdS/RuO₂ and a u-oxo complex for stoichiometric splitting of water. 'L' is ethylenediaminetetracetate ligand.

Thus *in situ* formed ZnS colloid is reported to photocatalyse hydrogen evolution from H₂O in presence of sacrificial electron donors such as MeOH, EtOH and THF. The production of H₂ (0.50 ml/h) is reported to be stable even after 22 h operation. In another study by Reber and Meir³⁹ with ZnS in electrolyte solution (90 ml) containing sacrificial electron donors which was exposed to UV light at 60°C, a quantum yield of 0.90 has been reported for H evolution. This system has been claimed to produce about 15 liters of hydrogen in about 34 h of irradiation. The performance of these simpler ZnS-based systems is far more superior to model systems constructed based on those shown in Figure 3.

Hydrogen sulphide (H₂S), like water, is another potential source of hydrogen. Photocatalytic dissociation of H₂S is highly desirable from the point of view of product value as well as waste utilization. First observation of H₂S photodissociation over CdS has been made by Borgarello and coworkers⁴⁰. These authors^{41,42} have subsequently reported quantum efficiency of H₂ evolution about 0.45 and overall energy conversion efficiency about 3%, for Rh/CdS catalyst in an alkaline solution of H₂S and SO₂. The photodecomposition of H₂S over CdS may be mechanistically exemplified as shown in Figure 5. Polysulphide (S_m²⁻) formation (shown in Figure 5) needs to be suppressed for enhanced hydrogen production for which sulphite addition is found to be useful. Serpone *et al.*⁴³ have used the principle of interparticle electron transfer between two different types of semiconductors to accomplish visible light-induced decomposition of H₂S. Hydrogen evolution from H₂S has also been reported using Rh/CdS⁴⁴, CdS/RuO₂ supported on polycarbonate matrix/glass beads⁴⁵, ZnFe₂O₄⁴⁶ spinel catalyst, RhS/CdS⁴⁷, Cd/RuO₂⁴⁶ and Pt/CdS⁴⁹.

Photocatalytic systems that utilize light energy to produce ammonia from nitrogen and water form an

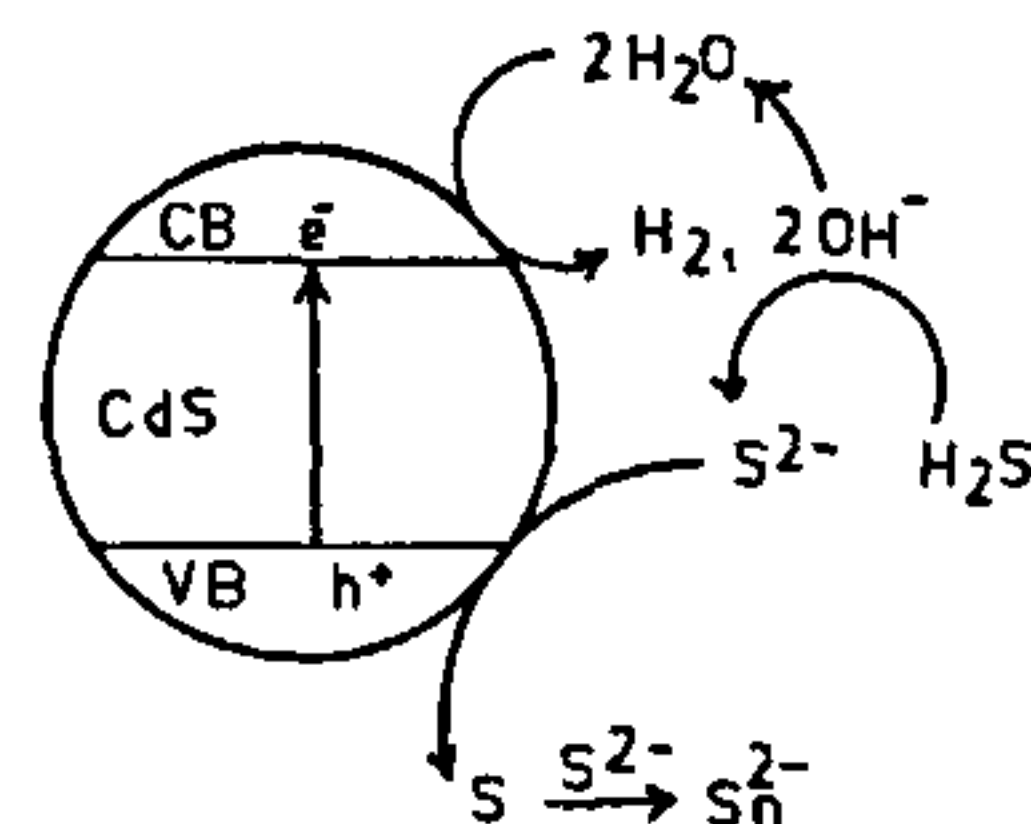


Figure 5. Hydrogen evolution from aqueous sulfidic media over illuminated CdS containing appropriate metal deposit (e.g., Rh) where sulfide oxidation and water reduction cycles are coupled.

important area of research. Originally, sand from coastal areas of California, Arabia, India and China was found to contain titanium which was shown to act as catalyst for ammonia formation upon exposure to sunlight in humid atmosphere⁵⁰. This finding, while establishing the ecological significance of sand in nitrogen reduction, also indicated the possibility of photocatalytic nitrogen reduction over sand where a part of the activation energy is provided by light. Following this the first observation of nitrogen reduction over illuminated TiO₂ and Fe doped TiO₂ has been reported by Schrauzer and Guth⁵¹. They have shown that photolysis of chemisorbed water over degassed TiO₂ (rutile powder) yields H₂ and O₂ in 2 : 1 ratio in Ar atmosphere. Introduction of N₂ gas is found to strongly inhibit the H₂ evolution only; this effect is more pronounced with Fe-doped TiO₂. This is attributed to dinitrogen reduction which used up photoproduced hydrogen. They proposed a mechanism wherein both water-splitting and nitrogen reduction are shown to occur simultaneously. The 2e⁻ water reduction process has lower activation energy (per electron transferred) than the 6e⁻ nitrogen reduction; chemisorption of both H₂O and N₂ over TiO₂ catalysts is suggested to be essential for the catalytic process. Following this the possibility of photocatalytic fixation N₂ over a number of semiconductors is stirred up. Many studies have reported photocatalytic reduction of nitrogen using TiO₂ or Fe doped TiO₂⁵², TiO₂ supported catalysts⁵³, Cu₂O⁵⁴, MoO₃⁵⁵, metal sulfides⁵⁶, Fe₂O₃ and hydrous ferric oxide⁵⁷, WO₃ based catalysts⁵⁸, Mg doped TiO₂^{52h}, p/n junction type doped Fe₂O₃⁵⁹, super acid⁶⁰ catalyst α-Fe₂O₃ · Nd₂O₃ · SO₄²⁻, SrTiO₃ incorporating oxides of Fe, Eu, and Tb⁶¹, hydrous Fe₂O₃ (nanoparticles) in naion films⁶², Fe compounds in the presence of Li poly(p-phenylene)^{57d}, Sm(III), Eu(III), and V(III) substituted Fe₂O₃ · H₂O^{63,64}, Mo(III-V) hydroxide/Ti(OH)₃⁶⁵, and Ti³⁺ exchanged zeolites⁶⁶.

The problem of photocatalytic nitrogen reduction has been approached in a different way in our own studies where aqueous solutions of ruthenium aminopolycarboxylato dinitrogen complexes comprising of metal

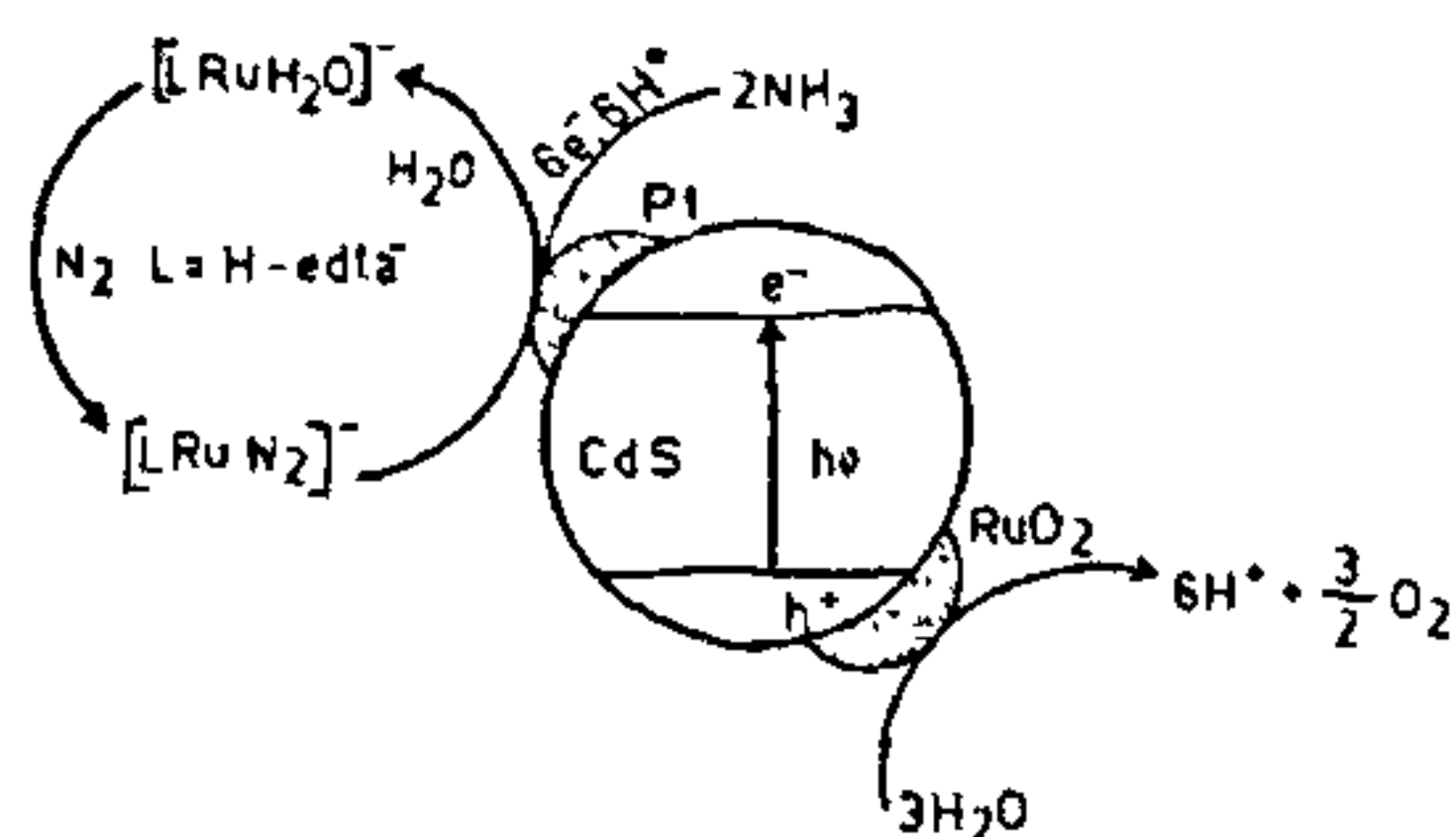


Figure 6. A scheme showing photocatalytic reduction of coordinated dinitrogen to ammonia using Pt/CdS//RuO₂ bifunctional redox catalyst. The complex reduction cycle in the left is coupled to water oxidation half cycle in the right.

chalcogenide particles were illuminated with visible light. The underlying idea of using transition metal complexes of dinitrogen is to lower the activation energy for the transfer of electrons thus facilitating reduction of nitrogen. The catalytic reduction of coordinated dinitrogen in [Ru(HEDTA)N₂]⁻ over Pt/CdS/RuO₂^{56a,b} has been demonstrated using visible light. The mechanism of photocatalytic reduction of nitrogen is believed to be as shown in Figure 6, the catalytic nature of this system is primarily attributable to the ability of the metal complex to bind nitrogen reversibly. Later it has been shown that there is no need to isolate the dinitrogen complex in separate experiment, instead it may be generated *in situ* employing CB electrons of illuminated CdS^{56c}. This system produces significant quantities of ammonia in presence of sacrificial electron donors like EDTA. It was further shown that when the semiconductor in the Pt/CdS/RuO₂ incorporates doped Ag₂S, the yield of ammonia is enhanced^{56d}. Through the detailed spectroscopic studies^{56d} the N≡N bond in [Ru(HEDTA)N₂] has been shown to undergo stepwise reduction via hydride, diazido, and hydrazido intermediates. In continuation of the above work it also has been found that the photocatalytic reducibility of dinitrogen is a function of Ru^{II}/Ru^I redox couple^{56e}. On an average, a turnover number of 6–10 can be demonstrated with the [Ru(HEDTA)N₂]/CdS/visible light system operable stably for 6–10 hours. This is significant compared to the amounts of ammonia obtainable photocatalytically when merely various semiconductors were used.

Two reasons appear to be responsible for the poor efficiency: the N₂ adsorbing properties of oxidic semiconductors are not optimum and the probable slow transfer of (H)_{ads} to N_{2ads}. It appears that the use of the dinitrogen complexes adsorbed on the semiconductor surface through their loose COO⁻ groups and the reversible binding nature of N₂ under ambient conditions seems to offer a greater advantage. The coordinated dinitrogen in such adsorbed complex may

be reduced catalytically provided the CB electrons are effectively transferred to Ru metal centre. Despite these advantages with photocatalytic systems that incorporate reduction of coordinated nitrogen, their performance is still unsatisfactory as they are not spared from either degradation of metal chalcogenide or complex side reactions in which Ru complex is shown to participate.

Besides photocatalytic reduction of nitrogen, oxidation reactions of chemisorbed nitrogen also appear to be feasible on illuminated TiO₂ surface^{50,67}. The oxidation product (NO) of nitrogen has been detected by Bickley and Viswanathan⁶⁷ upon illuminating TiO₂ powders (pretreated with H₂O₂) in the gas phase. In experiments with TiO₂ in aqueous medium⁵⁰ only nitrite (NO₂⁻) ions have formed, however with TiO₂ pretreated with H₂O₂ both nitrite and nitrate have been reported. As TiO₂ promotes photooxidation of NH₃⁶⁸, initially formed ammonia by photocatalytic reduction of N₂ may participate in oxidation reaction. In fact, the decrease in NH₃ concentration frequently observed after reaching a maximum in a number of nitrogen photoreduction experiments, has been attributed to simultaneous oxidation of NH₃ formed⁶⁹. These studies⁶⁹, however, have shown that TiO₂ catalysts coated with Ag, Hg, and Pt produce ammonia predominantly, while ZnO produces only nitrate. Oxidation of coordinated nitrogen in [Ru(HEDTA)N₂]⁻ over UV irradiated Pt/TiO₂/RuO₂ in aqueous solution has been reported⁷⁰ by us; here, anatase catalyst is found to be superior (by about 25–30 times) and a mechanism showing surface oxygen atom transfer to adsorbed dinitrogen complex has been proposed. A composite ZnO–Fe₂O₃ catalyst has also been reported to photooxidize N₂ to NO₂⁻ in aqueous solutions⁷¹.

Conversion of carbon dioxide into C₁-chemicals using solar energy is of great significance. The process of photocatalytic reduction of CO₂ to a variety of products⁷² has been reported using suspensions of semiconductor particles such as SiC, GaP, CdS, TiO₂, SnO₂, and WO₃ in aqueous carbonate solutions⁷³. Various reduction products of CO₂/CO₃²⁻ have been reported (e.g., carbon, methane, formaldehyde, methanol, formic acid, carbonmonoxide, and isocitric acid) using Pt/TiO₂⁷⁴, α-Fe₂O₃, Zn–Fe oxide, Co–Mo oxide, Pt/La–Ni oxide catalyst Pt/SrTiO₃⁶⁴ Co–Mo–Al-oxide catalyst⁷⁵, enzyme coupled CdS⁷⁶, Cu and TiO₂ or Cu/TiO₂⁷⁷, Cu(1%)/ZrO₂⁷⁸, TiO₂ anchored to vycor glass⁷⁹, silica-supported Fe⁸⁰ and poly(3-alkylthiophene) films⁸¹. The strategy of combination of homogeneous catalyst that activates CO₂ by coordination and illuminated semiconductor surface which acts as a pool of redox species has also been applied to photocatalytic reduction of CO₂. Thus the system⁸² comprising Ru-aminopolycarboxylate complex, Pt/CdS/RuO₂ and dissolved CO₂ produces HCOOH and HCHO on illumination at λ = 505 nm. While it is clear that the

photocatalytic route for carbondioxide reduction into C_1 -chemicals is feasible, enhancement of their yields as well as selective reduction of CO_2 to the required C_1 -chemicals should be attempted.

Photocatalytic oxidation of pollutants

Photocatalytic oxidation (PCO) of water-bound environmental contaminants by semiconductor powders irradiated with solar or simulated light is a comparatively new method for the destruction of toxic chemicals in water⁸³. The objective here is to effectively mineralize organic contaminants i.e. convert them into carbon dioxide, water and oxidized inorganic anions (if any heteroatoms present). It is preferable to classify the published literature according to the class of the contaminants: halohydrocarbons, surfactants, dyes/dye-stuffs, oils, cyanide, trace noble and/or toxic metals.

Halohydrocarbons are widely used solvents, pesticides, insecticides and herbicides and pose severe environmental hazard even in very low concentrations in water. The higher the number of halogen atoms in a molecule, the higher is its toxicity. These substances are not readily degraded or hydrolysed in normal aquatic environment. Titanium dioxide can be used to completely photodegrade simple chlorinated hydrocarbons into CO_2 and HCl ⁸⁴⁻⁸⁸. Among the compounds studied are dibromoethane⁸⁹, trichloroethylene⁸⁸, chloroacetic acids and chlorobenzenes^{87,90}, chlorophenols⁹¹, benzoic and salicylic acids^{92,93}, PCBs⁹⁴, trichlorophenoxyacetic acid⁹⁵ and chloromethane⁸⁴. A review on environmental photochemistry of chlorinated aromatics is presented by Cesareo *et al.*⁹⁶. Some volatile organic pollutants (such as TCE and PCB) can be removed from waste gas/air/water by PCO using TiO_2 , ZnO , SnO_2 , ZrO_2 , CeO_2 , WO_3 and Fe_2O_3 ⁹⁷⁻¹⁰⁰. Chlorobenzenes are found to be harder to destroy, while totally halogenated fluorotrichloromethane and 1,1,1-trifluoro,2,2,2-trichloroethane did not show any significant degradation¹⁰⁰. Recently we have found that TiO_2 is a better catalyst for the destruction of 2,4-dichlorophenoxyacetic acid, while MoO_3/TiO_2 is better for the destruction of parachlorobenzene¹⁰¹. Complete mineralization of 50 ppm solution of TCE containing 0.3% TiO_2 in a quartz recirculating reactor is reported to be possible in solar light in 2-3 h time⁸⁶. The participation of photoproduced $(OH)_{ads}$ on TiO_2 surface is conclusively shown^{102,103} in the photocatalytic degradation of organic contaminants. The possibility of considering photocatalytic oxidation to be an alternative to known water treatment methods has been proposed^{104a}. However, there exists possibility to generate highly toxic phosgene due to incomplete photooxidation of trichloroethylene over TiO_2 catalysts^{104b} in the photocatalytic reactions.

Surfactants pose severe ecological problems as their biodegradation is often too slow and inefficient. Anionic^{105,106}, cationic¹⁰⁷ and non-ionic^{108,109} surfactants can be destroyed under solar or simulated sunlight in the presence of aerated aqueous TiO_2 suspensions. A mechanism of photocatalysed destruction of surfactants is proposed by Hidaka *et al.*¹¹⁰. In general, anionic surfactants are easier to degrade, while any side chains present react slower than the aromatic groups^{110,111}.

Photocatalytic destruction of different classes of organic dyes using highly concentrated solar light and TiO_2 suspension has been reported¹¹² where heteroatoms such as S and N in the dye molecules transform into SO_4^{2-} and NO_3^- . Mineralization is reported to vary between 80 and 100% in <30 min irradiation. This work suggests that potential exists for the use of highly concentrated solar light in the destruction of textile dyes and biological stains from waste waters.

Photocatalysed oxidation of crude oil residue/oil slick by beach sand¹¹³ and hollow glass beads coated with TiO_2 ¹¹⁴ has been reported. The ability of sandy beaches to slowly degrade the oil layers using solar light has been recognized.

Cyanide is frequently found in rinse water of steel industry, electroplating, gold extraction in mines and metal cleaning. Here, cyanide ion binds to prevailing metal ions and exists as metal complexes. Photocatalytic oxidation has been suggested to have sufficient potential to convert cyanide into less toxic oxidized products. Thus cyanide¹¹⁵ and ferricyanide¹¹⁶ can be degraded on irradiated TiO_2 suspensions. Removal of CN^- coupled to photocleavage of H_2S to form thiocyanate has also been reported^{117,118} using CdS/Rh . While cyanide oxidation to OCN^- over illuminated TiO_2 ¹¹⁹ is frequently found, some authors have recently¹²⁰ shown further oxidation of OCN^- to NO_3^- and CO_3^{2-} . This work suggests the possibility of direct oxidation into non-toxic products of native elements in CN^- without having the risk of producing OCN^- which is only relatively less toxic compared to CN^- .

The ability of irradiated TiO_2 to reduce metal ions to metallic state on its own surface¹²¹ has been exploited to remove toxic and/or trace noble metal ions from waste water¹²²⁻¹²⁴. Typically, about 80% removal was possible with respect to Cu from a plating industry effluent containing Cu, Fe, and Zn using TiO_2 and UV lamp or solar light¹²⁴.

Photocatalysis-nanoscale materials

In recent years research work in the area of particles of small size (10-100 Å) has received much attention. There has been quite intense work in the methodology of preparation and stabilization of these particles and studying their physical and chemical properties.

Stabilization of these particles has been a particularly intriguing problem, and some new routes to stabilize them have been developed. Several review papers¹²⁵ have dealt these aspects in detail. As atoms and molecules form clusters or aggregates there exists a particular situation when the small particles show properties different from those of the bulk materials. Particularly the electronic properties of these clusters depend on the cluster size, a phenomenon known as 'size quantization effect' i.e., the energy of the electrons becomes quantized. Depending on whether size quantization takes place in one, two or three dimensions, one can obtain quantum dots, quantum wires, or quantum layers respectively. Size quantization leads to significant changes in spectral, electrical and reactivity properties. Primarily this effect can be identified by its manifestation as a blue shift in the absorption edge of the materials (i.e., exciton energy). For instance, Figure 7 shows the effect on the absorption spectra of CdS in solution wherein for relatively smaller particles structured absorption spectra are obtained. A blue shift in the excitation wavelength implies that an electron-hole pair is bound by coulomb interaction and thus relaxation of photoinduced $e^- - h^+$ pairs should be slower in the quantized semiconductors. Therefore, enhanced photoconversion efficiencies are theoretically possible with nanosize semiconductor particles.

There have been a few reports on the photocatalysis reactions using nanoscale materials. Particle size effects of colloidal Pt catalysts¹²⁶ and Pt clusters on TiO_2 ¹²⁷ and other metal clusters (microelectrodes)¹²⁸ pertinent to light-induced hydrogen evolution have been established. Using small particles of Fe_3O_4 ($\approx 100 \text{ \AA}$) stabilized by surfactant solutions we have shown¹²⁹ that dinitrogen can be reduced to ammonia. Further, flash photoprecipitated Pt clusters (10–20 $\text{\AA}$ or 50–500 atoms) have been shown to photocatalyse water decomposition, a

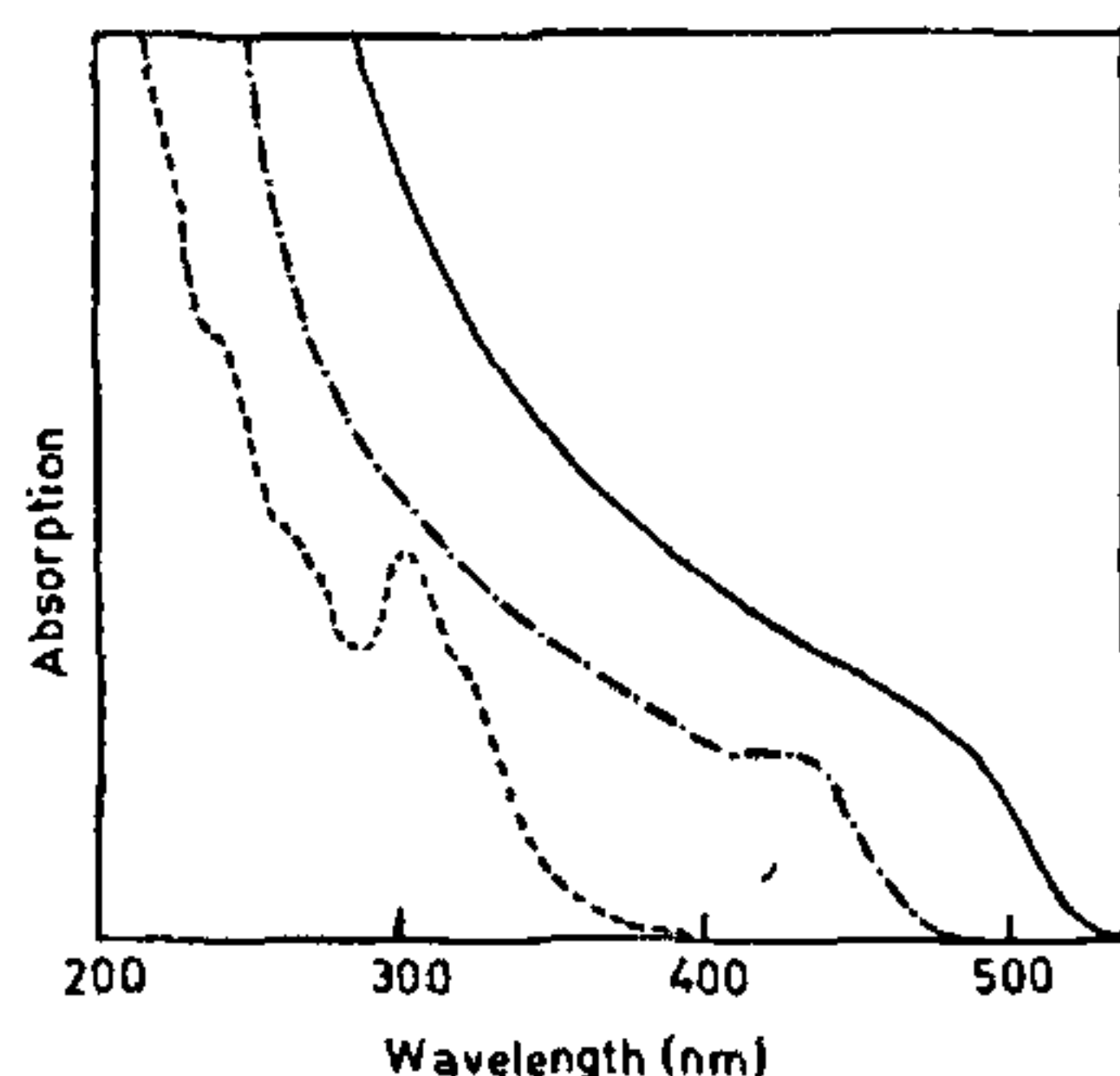


Figure 7. Illustration of the size quantization effect through absorption spectra of CdS colloids. Average diameter of colloidal particles — 2R 5 nm; - - - 2R 2.5 nm; - · - 2R 1.5 nm

sustained evolution of H_2 and O_2 is reported to be possible under visible light¹³⁰. A system containing Pt colloidal solstabilized by viologen polymer and nanoparticles of CdS (dia. $< 5 \text{ nm}$) has been shown¹³¹ to photolyse heavy water (D_2O) upon irradiation for 1 h. It has been reported that quantum size CdS (2–5 nm) particles catalyse the photoreduction of aromatic ketones and electron-deficient alkenes with triethanolamine as an electron donor under visible light¹³². From this survey in the field of nanomaterials we felt that there appears the need for more attention in the area of the application of these materials for photocatalytic reactions considering their attractive properties.

Photocatalysis – Organic reactions

Photocatalysis may also be applied to organic redox reactions^{9,133}. Electrons in the conduction band (or $(\text{H})_{\text{ads}}$ or superoxide radical anions, O_2^-) may be advantageously used for reduction of unsaturated bonds viz: $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{C}=\text{O}$; while holes in the valence band (or $\text{OH}\cdot$ or H_2O_2 formed thereby) can be used for the oxidation processes.

Photohydrogenation of alkynes and alkenes has been reported (sometimes accompanied by the fission of $\text{C}\equiv\text{C}$ or $\text{C}=\text{C}$ bond) over TiO_2 , Pt/TiO_2 ¹³⁴ and Pt or Ru supported CdS¹³⁵, products such as CO , CO_2 , CH_4 and C_2H_6 have formed. Metal colloid-sensitizer-electron relay system has been also applied for photohydrogenation of unsaturated organic substrates such as styrene, cyclohexene, acrylonitrile, benzylchloride and cyclohex-2-en-1-one¹³⁶. We have reported¹³⁷ the hydrogenation of cyclohexene in aqueous ethanolic solutions of $\text{K}[\text{Ru}(\text{HEDTA})\text{Cl}] \cdot 2\text{H}_2\text{O}$ over illuminated Pt/CdS/RuO_2 . On the other hand, examples also exist for photocatalysed dehydrogenation reactions. Formation of ethylene and acetaldehyde from ethanol and HCHO from CH_3OH , acetone and isobutene from *t*-butanol, isobutyraldehyde from isobutanol and corresponding ketones from 2-propanol and 2-butanol has been reported¹³⁸.

In addition the photocatalysis may be applied to various organic oxidations. The well known water-gas-shift reaction may be photocatalysed over TiO_2 powders¹³⁹ and $n\text{-ZnS}$ ¹⁴⁰. In a reaction between carbon and H_2O over illuminated Pt-TiO_2 , products H_2 , CO_2 and small amounts of O_2 are reported to have formed¹⁴¹. In liquid phase, oxidation of carbon is reported to be inhibited. Many hydrocarbons such as benzene, hexane, cyclohexane, heptane, nonane, decane and kerosene have been reported to be oxidized over Pt-TiO_2 and porphyrin modified TiO_2 powders¹⁴². Recent reports¹⁴³ suggest that fullerenes get oxidized under UV, visible or laser irradiation in the presence of TiO_2 powders. The photoproduct, fullerene epoxide (C_{60}O) has been isolated.

Illumination of platinized TiO_2 dispersions in aqueous-aliphatic acid mixtures has been reported to produce hydrocarbon and CO_2 ¹⁴⁴ which is the well-known photo-Kolbe reaction. Compounds such as benzoic acid yield CO_2 and phenolic resin polymers, instead of usual Kolbe products¹⁴⁵. Dicarboxylic acids such as adipic acid have been found to react under similar conditions to yield CO_2 and butane. Ethane is the product of vapour phase photocatalysis of acetic acid¹⁴⁶. Sakata¹⁴⁷ has described the mechanisms of these photo-Kolbe processes under various conditions.

Several authors¹⁴⁸ have observed photoisomerization reactions while investigating reactions of alkenes over wet TiO_2 powders; the photocatalytic butene (but-2-ene to but-1-ene) isomerization is reported to be more efficient.

Formation of certain amino acids/peptides over irradiated Pt- TiO_2 ¹⁴⁹ and CdS¹⁵⁰ powders suspended in ammoniacal solutions saturated with methane has been reported. Further, photochemical nucleic acid base (hypoxanthine) formation when Pt loaded TiO_2 or Pt-CdS suspensions in aqueous solutions of KCN and NH_3 are illuminated¹⁵¹ and photoformation of polypeptide from glucose-ammonia-water over Pt- TiO_2 has been documented¹⁴⁷.

Depending upon the method of preparation of the semiconductor catalyst, the performance of the photocatalyst varies. In particular it has been observed that the rutile phase is active or inactive according to the preparative conditions¹⁵². The reactivity and application aspects of photochemistry and photocatalysis on semiconductor surfaces have been reviewed recently¹⁵³. An example of specificity of photocatalyst to a given reaction may be mentioned here. The photocatalytic reaction of lactic acid in H_2O is reported to yield hydrogen, carbon dioxide and acetaldehyde with Pt/ TiO_2 catalyst, while hydrogen and pyruvic acid are the products with Pt/CdS¹⁵⁴.

Recently, extra fine semiconductor particles have joined the list of common additives used to cause rapid degradation of polymers. For example, the low and high density polyethylene films (50–170 μm) containing 0.125–1.0 w/o TiO_2 (≈ 20 nm) degraded in UV light in about 200 h at ambient conditions¹⁵⁵. Further, linear accumulation of CO groups in the film upon illumination indicated the chemical transformation of polyethylene chain with the properties such as transparency and mechanical strength being also effected.

The principles of photocatalysis have been extended to develop light images with TiO_2 particles¹⁵⁶ and generation of metallic patterns over TiO_2 or TiO_2 sol adhered to alumina¹⁵⁷.

Photocatalysis: Views and prospects

Many studies have been carried out with the aim of either developing models of practical interest or

attaining more refined understanding of the functioning of the photocatalyst. Surprisingly, many simpler systems such as ZnS colloids for H_2 evolution and ion-exchangeable potassium niobates for water decomposition perform with much better efficiency than the systems constructed based upon models in Figure 3a–d. The efficiencies reported should be indicative of only the occurrence of photocatalytic reactions since their absolute comparison may not be informative as many parameters associated with any chosen system such as catalyst pretreatment, electrolyte composition, source of light etc critically effect the yields. The expanding area of the field of photocatalysis as illustrated especially for applications in organic chemistry, light images, metallic patterns and pollution treatments, however, makes us to believe the prospect of wide applicability of photocatalysis. Aspects such as water-splitting, dinitrogen fixation, carbon dioxide reduction, hydrogen evolution from sulphidic media continue to receive attention. The areas of application of photocatalysis to water purification and treatment of water, area selective reactions polymer degradations and selective organic synthesis will probably gain priority as they appear to possess the potential to alter environmental and electronic scenarios.

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Space and physical sciences

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Being a physicist, having close links with space efforts of the country, I propose to use this opportunity to share with you the excitement of doing physics the space-way. Over the last three decades, we are witnessing a phase of science research where breakthroughs or opening of new frontiers of knowledge are becoming increasingly possible only with advances in experimental techniques and technology with technological and scientific advances driving each other. Here I propose to cite some specific examples of fundamental contributions to physics made possible by advances in space technology, a more exhaustive list of which is given in Table 1. I shall also discuss the possibilities of doing experiments in physical sciences using the Indian space platform.

Contributions in high energy astrophysics

Introduction

With the advent of space exploration, new windows in the electromagnetic spectrum namely, gamma ray, X-ray, extreme UV and several regions of IR have been opened up for detailed investigation from space platforms. The birth and growth to maturity of X-ray and IR-astronomy and more recently gamma ray astronomy through satellite missions like Uhuru, Einstein observatory, ROSAT, IRAS and Compton Gamma Ray Observatory are prime examples of this development. I shall choose a few topics in X-ray astronomy, to highlight the significant results that have emerged out of the above investigations.

Observational X-ray astronomy was born with rocket-borne experiments way back in 1962 and matured with the launch of the first X-ray astronomy satellite UHURU in 1970. The observation of bright X-ray sources with luminosities ranging from 10^{36} to 10^{38} erg/s provided the opportunity to understand and investigate matter at extreme densities (10^{14} to 10^{15} g/cc) with very high surface temperatures (> million K) and very strong magnetic fields ($\sim 10^{12}$ G).

Basic understanding of the physical processes of accretion of matter by compact stars having intense gravitational potential came about from X-ray astronomy. Most of the bright X-ray sources are found to be in binary systems where one of the stars is a

compact object (white dwarf, neutron star or a black hole) which accretes matter from a companion star which is more evolved than the Sun. The infalling matter acquires a large kinetic energy as it falls on to the surface of the compact object and this energy is released as radiation.

The mass loss from a supergiant companion star can be typically $\sim 10^{-5} M_{\odot}$ /year. Even if 0.1% of this matter gets accreted on to a neutron star, the transfer of matter, at a rate of $10^{-8} M_{\odot}$ /year, with a mass to energy conversion efficiency of 10% can give rise to luminosities of the order of 10^{38} erg/s. This is 10^5 times the total luminosity of the sun and is 10^9 times the X-ray luminosity of the sun. Such high energy liberated around a small-sized object like a neutron star can only be carried away by high energy photons and thus these objects appear as bright X-ray sources.

I shall now discuss two cases where X-ray observations from space have enabled us to make one of the first measurements of the mass of a neutron star and the first identification of a candidate black hole.

Determination of the mass of a neutron star

The object I choose for this purpose is Her X-1 which is the brightest X-ray source in the constellation of Hercules. Discovered by the Uhuru satellite, it exhibits short timescale pulses with a period of about 1.24 seconds both in the X-ray and optical wavelengths, attributed to the rotation of the compact object. The pulsations are caused by the accretion of matter on to the magnetic poles of the compact object, whose magnetic axis is tilted with respect to its rotation axis.

The Doppler shift observed in the 1.24 second X-ray pulsations provides the radial velocity curve of the binary system and this curve being sinusoidal, indicates

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