

METAL CHALCOGENIDE NANO-PARTICLES BASED MULTIPLE PHOTO-CATALYSIS IN DAILY LIFE

Abstract

Development of innovative nano-sized materials for multi-functional photo-catalysis application is gaining extraordinary importance worldwide. In this sense, several metal chalcogenides nano-particles (NPs), such as TiO_2 , ZnO , CuO , Fe_3O_4 , FeS , ZnS , CdSNPs etc. and their composite have been synthesized and established as effective heterogenous recyclable catalyst for conducting several photo-chemical applications to the society. When the nano-particles have capability to absorb solar light energy, the performance for photo-catalysis has been increased much more. In this chapter it has elaborated that how the light energy even solar energy can be used to drive interesting technologies to be utilised in daily life and everyday consumer products. It has been also been presented detailed information on a photo-catalysis based number of commercial products such as hydrogen-fuel generation devices as alternative energy source from water splitting, environmental pollution remediation and technology through degradation of pollutants, air purification devices, UV-protection and self-cleaning techniques on textile-clothing solar panel, self-cleaning glasses, tiles, paint materials etc.

Keywords: Photo-catalysis, semiconducting nano-materials, light-driven chemical reactions, hydrogen-fuel, waste-water treatment, air purification, self-cleaning.

Author

Dr. Amit Kumar Dutta

Department of Chemistry
Bangabasi Morning College
19 Rajkumar Chakraborty Sarani,
Kolkata, India.

I. INTRODUCTION

Photocatalysis is one of the most useful methods where photo-energy is used to conduct a chemical reaction [1]. The name 'Photo-catalysis' is a mixture of two words: 'Photo' connected to Photon or light and 'Catalysis', in which is a chemical reaction speed is generally increased in presence of a catalyst material. Here, the light energy is the driving force for conducting a chemical reaction. Light is an outstanding source of energy; it can give life to plants as well as power to our bodies. When solar light energy is used in a photo-chemical reaction, it will be most useful alternative sustainable energy source as the abundance is virtually unlimited and free [2]. So, effort needs to be done on enlightening environmentally-friendly and cost-effective technologies for fully utilizing this powerful unlimited resource for the sake of society. Now-a-days, with tremendous development of science and technology, so many photo-catalysis research works have been devoted on innovation and development of interesting technologies to be utilised in daily life and everyday consumer products. In the field of environmental pollution waste-water treatment and air purification, photo-catalysis process has already been utilised world-wide for complete degradation of organic pollutants in presence of a nano-catalysts material under light illumination. Very recent, photo-catalysis has been widely applied for hydrogen-fuel production as alternative non-carbon energy source. Nanotechnology-based photo-catalytic self-cleaning surfaces coating have widely been used in exterior building construction materials, tent-materials, in which sunlight or indoor light have been used to decompose pollutants that can be washed away with rain/water. Some commercial painting materials mixed with photocatalysis technology have been widely utilised for degradation of air pollutants even carbon monoxide (CO), nitrogen and sulphur containing organic compounds (NO_x) under light irradiation. Besides, Nano-catalysts thin films coating roof-tiles, concrete, glass windows, anti-fogging and anti-reflecting glasses, white cement containing nanoparticles, visible light active glazed ceramic tiles, even medical products and food products with photo-induced antimicrobial action have been extensively used throughout the world. Also, photo-catalysis technology provides us UV-protective, heat-resistant fire-fighter's suits, coffee or red wine stains-resistant garments etc. In the year of 1967, Prof. Fujishima and Honda of Tokyo University of Science, Japan, first discovered the photo-catalysis technology which is basically analogous to the naturally occurring photo-synthesis technique in plant leaves and similar types of photo-chemical reactions have been carried out under light irradiations (Figure 1). In their research works, it has been observed that, in a photo-electrochemical set up with Titanium dioxide (TiO₂) working electrode and Platinum counter electrode, when light was fallen on the TiO₂ electrode, gas bubbles have been evolved from the surface of the electrode and the bubble evolution has been stopped when light was switched off [3]. It has been confirmed that the bubbles consisted of hydrogen gas has been generated on the surface of TiO₂ working electrode and simultaneously oxygen gas has been generated at the Pt counter electrode from water splitting. Since, their successful research, so many nano-technology based photo-catalysis research works has widely been devoted for development of interesting technologies such as hydrogen-fuel generation as alternative energy source from water splitting, carbon-di-oxide reduction to hydro-carbon fuels, environmental pollution remediation through degradation of pollutants, air purification, UV-protection and self-cleaning on textile-clothing etc. in presence of a catalyst material under light illumination for the sake of society [5].

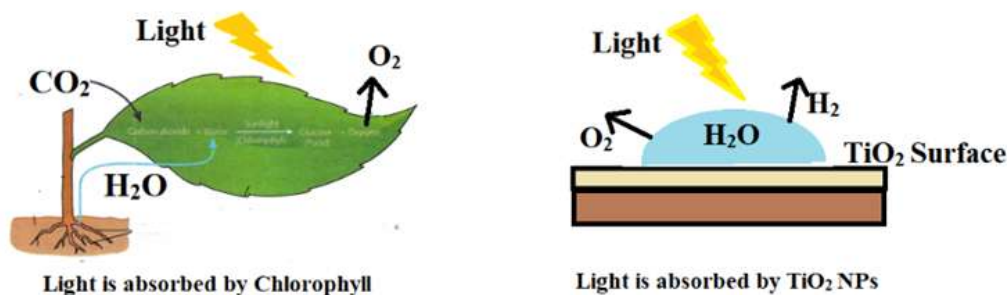


Figure 1: Photo-Catalysis Technology on TiO₂ Surface, Basically Analogous to the Photo-Synthesis Technique in Plant

As a catalyst material, nano-sized inorganic materials show remarkable efficiency in the field of photo-catalysis technology. The dimension of that materials is so small (nano-scaled level) and hence new interesting chemical and physical properties have been generated such as large specific surface to volume ratio, greater surface tension, greater surface activity, high catalyst loading capacity and better light absorption capacity. When the nano-materials are semiconducting in nature, they possess appropriate band gap energies and band-potential levels that can easily absorb light energy and quicken the photo-chemical reaction pathway [5]. Most of the metal chalcogenides nano-particles such as metal oxides, metal sulfide TiO₂, ZnO, CuO, Fe₃O₄, FeS, ZnS, CdSNPs etc. are semiconducting in nature and have proper redox potentials, excellent electron transfer ability and outstanding stability in air and solutions [6]. Again, they are easily available, non-toxic, and chemically stable for long time and have unique optoelectrical properties, suitable band gap energy to absorb UV, visible, even solar light energy. Over the past decade, TiO₂-based semiconducting nano-materials are well-known catalyst and widely used in photo-catalysis applications, mainly due to its photo-chemical stability, high oxidation power, high resistance to photo-corrosion in aqueous environments, safety, and lower cost than other photo-catalytic materials, however, it is catalytically active only under UV irradiation ($\lambda < 400$ nm) because of its wide band gap energy ($E_g \approx 3.2$ eV) [7]. Of late, several non-TiO₂-based materials such as ZnO, CuO, FeS, ZnS, CdSNPs etc. and even doped hetero-nanostructures Bi₂S₃/ BiOCl, Eu-doped Bi₂S₃ have been found to exhibit visible and solar-light-driven catalytic activity [8,9].

Keeping in mind the multiple photo-catalytic applications to the society, in this chapter, it has been discussed on details about the fundamental principle of photo-catalytic technologies based on different semiconducting nano-materials. The probable mechanism of the photocatalytic processes has also been explored through the detection of reactive oxygen species (ROS). How the proposed nano-materials have been commercialized for the sake of society based on their efficiencies and availability in different field such as in photo-active devices for purification of waste-water, hydrogen-fuel generation as alternative energy source from water splitting, self-cleaning of deposited dust or contaminant particles from surfaces, air purification have been deliberated. This chapter also presented information on a photo-catalysis based some commercial products such as solar panel, self-cleaning glasses, tiles, paint materials etc.

1. General Mechanism of Photo-Catalysis: In photo-catalysis process, metal chalcogenide-based nanomaterials are so chosen as heterogeneous photocatalyst materials because they are semiconducting in nature and possess appropriate band-gap and band-potential levels with filled valance band maximum (VBM) and vacant conduction band minimum (CBM) (Figure 2). Titanium dioxide (TiO₂) nano-material has been preferred as the model catalyst material for basic investigation and to demonstrate general surface photocatalytic reactions of semiconductors. It is generally accepted that the main reactions responsible for photocatalysis are the interfacial redox reactions of carriers generated when a certain amount of energy is absorbed by the semiconductor catalyst. If the band-gap energy of the catalyst is equivalent or less than the energy of incident light energy, the electrons residing in VBM will absorb the photon and be promoted to the CBM, thus leaving behind hole in VBM of the semiconducting nanomaterials (Figure 2). As a result, electron/hole pairs (e⁻/h⁺) are generated. Many of them have a possibility for recombination but some could be separated at the surface of the semiconductor and that electrons are able to react with electron acceptors (O₂) and holes can accept electrons from water bodies to produce hydroxyl radicals (OH•) and other reactive oxygen species (ROS)[10]. These radicals actually convey the photo-chemical reactions.

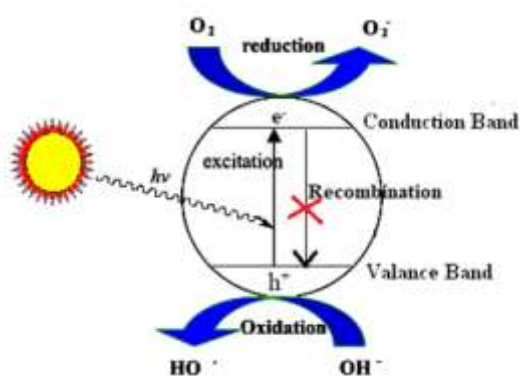
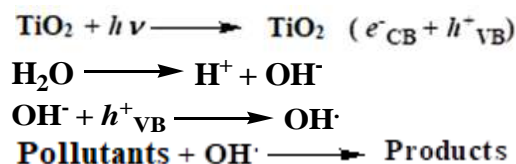
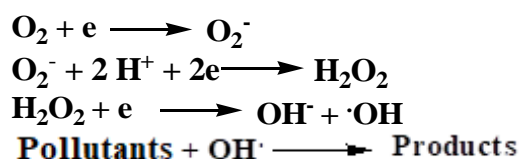


Figure 2: Illustration of Photo-Catalytic Mechanism

The overall reactions are presented in following equations.

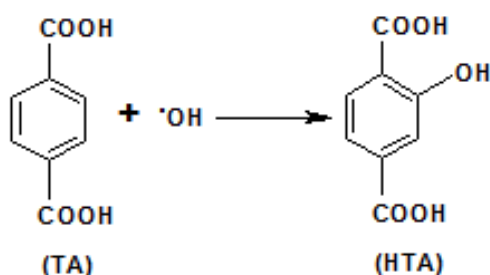


The environmental pollutants have also been degraded by other reactive oxygen species (ROS) such as O₂⁻ or superoxide radicals (O₂^{-•}), which have been produced on the surface of the nano-particles according to following equations.



As a whole, both O_2^- and OH^\bullet are responsible for photo-chemical reactions.

The in-situ formation of OH^\bullet has been established by terephthalic acid (TA) photoluminescence probing, which is usually used in detection of OH^\bullet radical generated in any chemical reaction [11]. In presence of nano-catalyst and on exposure to solar or visible light, non-luminescent TA easily reacted with in-situ formed OH^\bullet and is transformed into highly fluorescent product, 2-hydroxy terephthalic acid (HTA) according to following equation.



If that band-gap energy in one semiconductor nano-catalyst becomes tremendous low, the lifetime of the produced e^-/h^+ pairs in its surface becomes also short, there is a possibility of the recombination of e^-/h^+ pairs and hence the photo-catalytic efficiency of that nano-catalyst is generally shown to be less. Adding dopants, impurities, composite structures onto that nano-catalyst can suppress the re-combination of electron-hole pairs, enhance their lifetime and improve photo-catalytic efficiency of doped nano-catalyst (Figure 2). The presence of dopants or impurities in the nano-catalyst encourages intra-band electron transitions, such as electrons moving from defect states to ground states. By adjusting the size, morphology and composition of impurities, intra-band gaps can be modulated.

In hetero-nanostructure, lattice mismatch arises in the hetero-junction area due to presence of different lattice spacing between two semiconductors and cause lattice defect as a whole. That defect can trap the photo-generated carriers; there by reduce recombination of electron-hole pairs. Again, lattice defect can also be generated in single metal oxide say ZnO nano-structure through oxygen vacancies and similar way increasing catalytic efficiency.

- 2. Photo-Catalytic Hydrogen-Fuel Production:** very recently, photo-catalysis has been widely applied for hydrogen-fuel production as alternative non-carbon energy source. This is the low-cost method and not evaluates harmful CO_2 gas, like natural fossil fuels (coal, oil, natural gas etc.), which makes serious impact on our environment is global warming. Inspiring from the first research-work of Fujishima and Honda in the year of 1972, where water have been decomposed into oxygen and hydrogen in photo-electrochemical (PEC) set up using TiO_2 electrode under light irradiation, now-a-days, so many researchers have paid considerable attention to increase hydrogen production efficiency in large scale way using efficient catalyst material even under natural solar-light illumination.

Similar to general mechanism of photo-catalysis discussed above, photo catalytic hydrogen production occurs through water splitting into H_2 and O_2 over a heterogeneous semiconductor photo-catalyst under light illumination and mild conditions according to equation

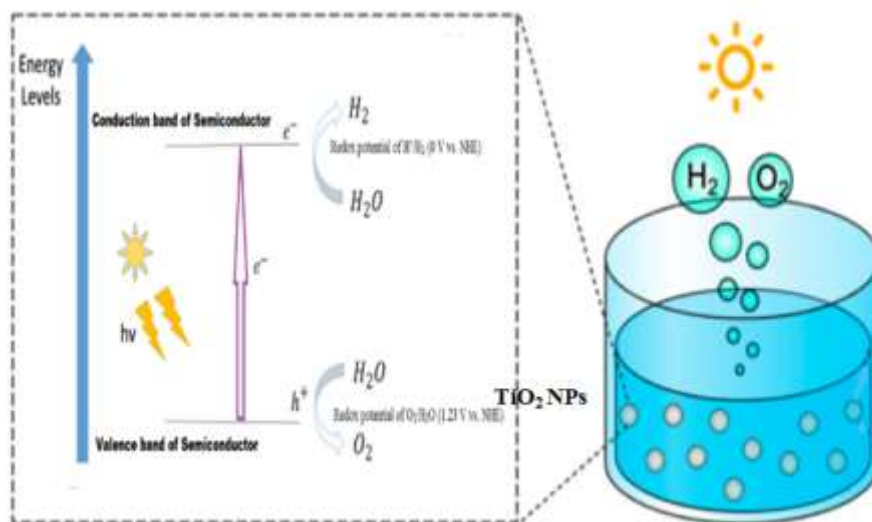
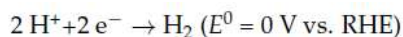
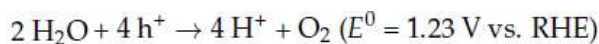


Figure 3: General Illustration for hydrogen and Oxygen Evolution on TiO_2 Nano-Catalyst

The photo-chemical reactions basically start from incident light energy activating semiconducting nano-catalyst followed by free electron-hole pair (e^-/h^+) formation. That electrons and holes have been transferred to the active sites of the surface of the nano-catalyst, acting as reducing or oxidizing agents to drive reduction or oxidation reaction on that surface. In water splitting process, water molecules have been reduced by the photo-induced electrons to form H_2 and have been oxidized by the photo-induced holes to form O_2 i.e., the Hydrogen evolution reaction (HER) and Oxygen evolution reaction (OER) have been occurred (Figure 3). The hydrogen gas produced was collected using gas-tight syringe and analysed by gas chromatography.

From the thermodynamic restrictions, a semiconductor photo-catalyst nanomaterials that has the ability to split water to produce hydrogen must have flat band positions in such a way that the bottom level of the conduction band (CBM) position should be more negative than the redox potential of H^+/H_2 (0 V vs. NHE) for evolution of hydrogen and the filled valence band maximum (VBM) needs to be more positive than the standard reduction potential of O_2/H_2O (1.23 V vs. NHE) for evolution of oxygen. So, the minimum band-gap energy of the semiconductor photo-catalyst for water splitting process requires 1.23 eV. Figure 4 represents the band potential positions of several metal chalcogenide semiconductors relative to the water redox potential levels which can efficiently split water to produce hydrogen. In case of TiO_2 photo-catalyst, the band-gap is large enough i.e., 3.0 eV, higher than 1.23 eV, to split water and also its band position matches well with redox potentials of water splitting.

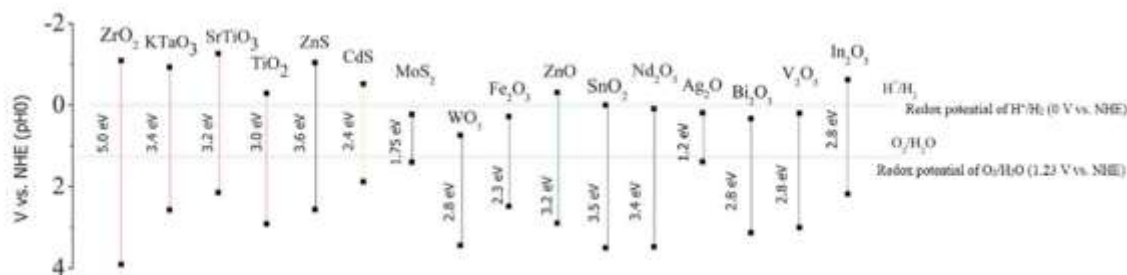


Figure 4: Band Potential Position of Several Metal Chalcogenide Semiconductors against Normal Hydrogen Electrode (NHE) as a Reference

Though fulfilling thermodynamic potential level restriction, some nano-materials cannot efficiently produce hydrogen because most of the photo-generated electrons and holes (e^-/h^+ pairs), that can migrate to the nano-catalyst's surface and responsible for protons reduction to form hydrogen, have been recombined on that catalyst's surface in a very short time. Again, after formation of hydrogen, the backward reaction of H_2 and O_2 to H_2O occurs immediately. In this case, instead of pure water, some specific chemicals have widely been employed into the water as hole scavengers such as methanol, ethanol, t-butanol, 2-propanol, d-glucose, Na_2SO_3 etc. Experimental measurement for photocatalytic hydrogen production has been carried out in a closed system of quartz catalytic reactor in presence of different nano-catalyst and methanol as hole-scavenger under natural sunlight irradiation [12]. The hydrogen gas produced was collected using gas-tight syringe and analysed by gas chromatography. According to R. Banerjee and her co-workers [13], the rate of hydrogen production over a heterogeneous photo-catalyst, CdS-carbon nano-composite (40 MC/CdS of Figure 5), has been found to be much higher i.e. $37,641 \mu\text{mol/g/h}$ due to presence of suitable flat band potential and photo-generated charge separation ability of the catalyst.

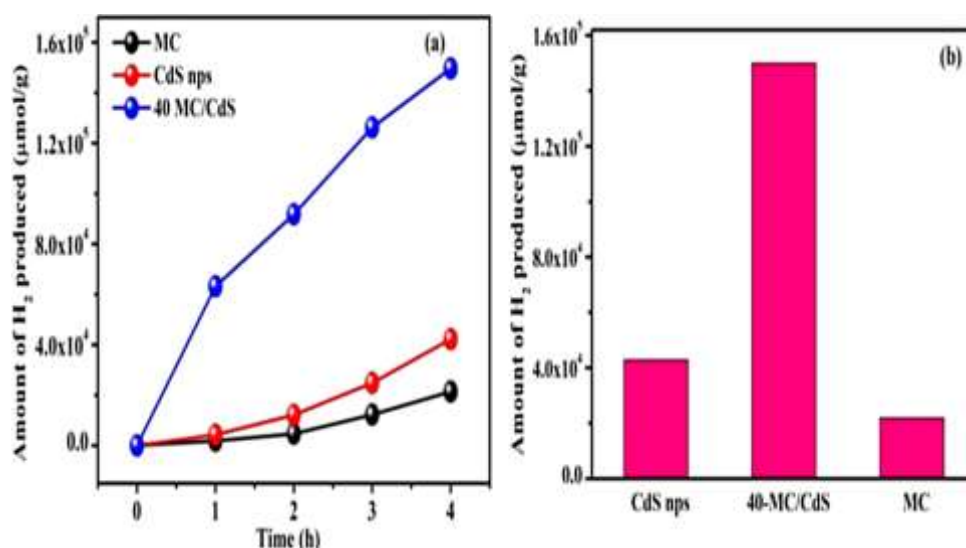


Figure 5: (A) Photo-Catalytic Hydrogen-Fuel Production (Mmol/G/H) In Presence of Different Cds Nps (B) Comparative Study Of H_2 production obtained after 4 H of Light Irradiation (R. Banerjee, 2021).

3. Photo-Catalytic decomposition and Remediation of Organic Pollutants in Waste-Water Treatment: In the waste-water treatment, photo-catalytic capability of the proposed metal chalcogenide nano-particles have been tested through decomposition of water soluble and non-biodegradable organic pollutants, Rose bengal (RB), methylene blue (MB) dyes or phenol-based pollutants under light irradiation. They have been chosen as example of environmental pollutants because they are commonly used in industries. The catalytic performances have been investigated spectro-photometrically through the degradation of MB in the wavelength range 550–750nm under light illumination. It has been shown that the absorbance (A) value at λ_{\max} position has been decreased rapidly with the irradiation time (Figure 6A) catalysed by Fe_3O_4 NPs and the corresponding solution became colourless (Figure 6Ainset) within few hours“unpublished” [14].

A comparative study has been illustrated in Figure 6B with Fe_3O_4 NPs and commercial TiO_2 (Degussa P25), where the degradation of MB has been achieved up to 99% with Fe_3O_4 nano-catalyst within few hours. It has also been established that enhanced photo-catalytic activities of the different nano-sized materials arises mainly due to presence of relatively smaller particle size, larger surface area, larger catalyst loading capacity and higher crystallinity nature.

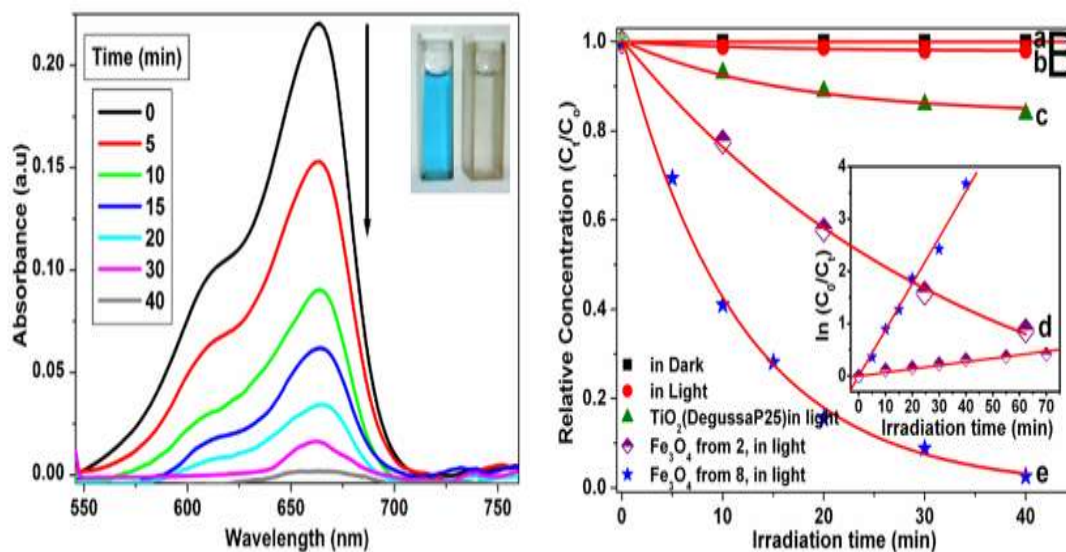


Figure 6: (A) UV-Vis Spectral variation of an Organic Pollutant, Methylene Blue in Water as a Function of Irradiation Time in Presence of Fe_3O_4 nano-Catalyst. Inset Shows the Photography of Corresponding Colour Change During Degradation Process, (B) Corresponding Kinetics Profile With Pseudo-First Order Modelling

To measure exact time taken for degradation and remediation of polluted water, the decomposition processes have been modelled as a pseudo–first order reaction kinetics expressed by the following equation

$$\ln(C_0/C_t) = k \times t$$

Where C_0 = initial concentration, C_t = concentration at a given reaction time ‘ t ’, and k = reaction rate constant. The data have been fitted to that kinetic model using a nonlinear least square fitting routine to obtain the rate constant values and summarized in Table 1

Table1: Kinetic Parameters for the Photo-Catalytic Activity of the Proposed Nano-Sized Materials.

Photo-catalyst	Rate constant with RB (min^{-1})	Rate constant with MB (min^{-1})
γ - Fe_2O_3	2.15×10^{-2}	8.80×10^{-2}
WO_3	3.3×10^{-3}	4.5×10^{-3}
TiO_2 (Degussa P25)	1.7×10^{-3}	1.16×10^{-3}
CdS	2.2×10^{-2}	–
ZnS	2.17×10^{-2}	–
FeS	–	2.71×10^{-2}
FeS	6.02×10^{-2}	5.73×10^{-2}
FeSe	3.39×10^{-2}	2.32×10^{-2}

4. Photo-Catalytic air Purification: Now days, several air-purifier devices have been developed to be utilised in daily life based on photo-catalysis, where air pollutants are converted to harmless substances in the presence of nano-catalyst under solar or indoor light irradiation. In these devices, photo-catalytic oxidation (PCO) technology has been incorporated to purify air where nano-catalyst material can oxidize the gaseous compounds such as carbon monoxide (CO), nitrogen and sulphur containing organic compounds (NO_x), volatile organic compounds (VOCs), other inorganic gases etc. that come into contact with surface of them [15]. Again, in case of indoor air pollution caused by different sources like the adhesives and building material’s discharge, the ignition (fire) processes in addition to the use of house-hold products, furniture, electric and electronic devices, VOCs can encourage damages to organs and metabolic systems or asthma and cardiovascular diseases. Now-a-days, some wall paints mixed with photo-catalytic materials have been widely applied for improving the air quality through degradation of volatile organic and inorganic pollutants present in air or deposited on paint surface. Some TiO_2 (Titania)-based nano-material as a thin film coating on a piece of glass or ceramic or aluminium metal substrate has been used as photo-catalysts. Similar to radical mechanism of photo-catalysis, electrons that are released on the TiO_2 surface (upon UV-light irradiation) interact with water molecules in the air to generate reactive oxygen species (ROS) such as hydroxyl radicals ($\text{OH}\cdot$) superoxide radicals ($\text{O}_2^- \cdot$) hydrogen peroxide radical ($\cdot\text{OOH}$) which can actually occur oxidation process to reduce contaminants. In case of VOCs, photo-catalytic degradation process has been carried out similar to organic dyes degradation in waste-water treatment and the bigger carbon-based organic pollutant molecules break-down into harmless Substances CO_2 and H_2O (Figure 7). A photo-catalytic degradation of gaseous acetone has been investigated by Yu-Hua Li and his co-workers[16] in a Pyrex-glass cylindrical batch reactor using

paints made of Fe-doped TiO₂ nano-particles under light illumination and the acetone degradation efficiency have been found to be of 46.2%, which could effectively control indoor acetone pollution.

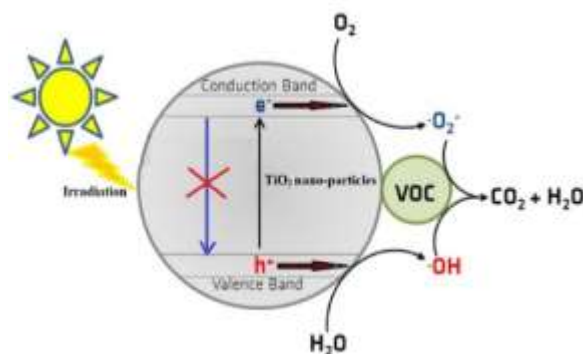
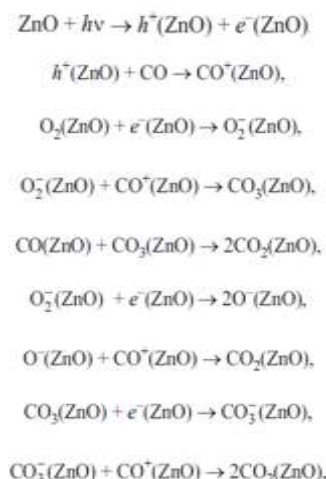


Figure 7: Illustration of Photo-Catalytic Oxidation (PCO) Technology of VOCs

Carbon monoxide (CO) is tremendous air pollutant, commonly known as silent killer that can cause both acute and chronic poisoning to human health. So immediate conversion to more harmless CO₂ or CO₃⁻ is necessary. Though the oxidation of gas phase CO into CO₂ is a thermodynamically favourable, but it requires high energy barrier i.e. Drastic reaction condition for oxygen dissociation. In this sense, photocatalytic oxidation of CO under light irradiation has become the best route for CO air treatment. That photocatalytic conversion has been extensively studied by Nagarjunan and Calvert [17] using ZnO samples, where oxygen was initially adsorbed on the ZnO surface, converted to ROS and as usual electron-hole pair on ZnO surface (upon light irradiation) can participate oxidation reaction. The proposed mechanism has been described as follows



During purification from H₂S or SO_x, Sulphur has been converted to sulfurtrioxide (SO₃) or sulfate (SO₄²⁻) and nitrogen containing organic compounds (NO_x) has been converted to nitrate or nitrogen gas through photo-catalytic oxidation process.

In comparison to air cleaner technology through simple filtration or trapping pollutants, photocatalytic air treatment shows big advantage, where all harmful molecules (exhaust fumes, have been completely decomposed and effectively destroyed. Even in case of indoor air pollutants such as volatile organic compounds (formaldehyde, acetaldehyde) evaporating from paints, hairsprays etc., photocatalytic chemically decomposition is the best route instead of removing them completely by sucking air polluted particles and blow clean out.

- 5. Photo-Catalytic UV-Protection and Self-Cleaning:** Following radical mechanism of photo-catalysis, photo-catalytic self-cleaning process of deposited dust or contaminant particles from any surface has become very popularise and commercialise through decomposition of the dirt and pollutants under solar light or indoor light irradiation. The photo-excited electron and valence band hole (h^+_{VB}) on the nano-catalyst surface can generate ROS that can convert dirt organic matter into CO_2 and water, resulting in the cleaning of the surface. Among the products based on solar photo-catalysis, the well-known TiO_2 , ZnO , SiO_2 -based self-cleaning surfaces have widely been used in exterior building construction materials, tent-materials, self-cleaning coatings for window glass, photovoltaic or solar panels with improved transmittance of natural sunlight and reflectance properties, since these materials are exposed to sunlight and natural rainfall.

Even in the textile industry, with the help of superior photo-catalytic and UV-light absorption properties of some semiconducting nano-materials, UV-protection and self-cleaning properties have been developed in semiconducting nano-particle coated textiles and clothing. TiO_2 or ZnO -type semiconducting materials have ability to absorb ultraviolet radiation and can protect the textile fabric from the harmful effect of ultraviolet rays. Also, our body gets protection by wearing sun-protective clothes made of semiconducting nanoparticle coated textile fibres. Moreover, when exposed to ultraviolet light, the photo-catalytic characteristic of the semiconducting nano-particle allows it to act as self-cleaning agent by photo-catalytic degradation of various colour stains (Figure 8). Even, photo-catalytic self-cleaning ability has been retained after several cycles of home-washing.

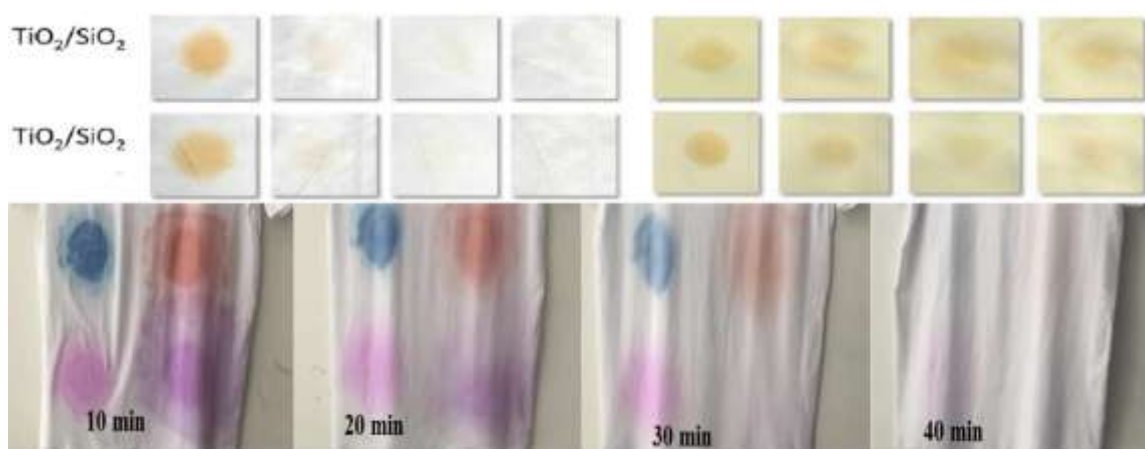


Figure 8: Self-Cleaning Observation of Fabrics with TiO_2/SiO_2 Coating under Light Irradiation

The self-cleaning efficiency of the nano-catalysts also depends on the basic surface properties such as adhesive and cohesive properties (hydrophobicity, oleophobicity and hydrophilicity).

Specially, super-hydrophilic nanomaterials-based surface coating can spread water droplets to form a film throughout itself and utilise solar light or indoor light to decompose any adsorbed organic contaminants such as oil, dirt etc. After that, the contaminants are wash-away with the help of water flow. Before construction of self-cleaning experimental set up, the wettability behaviour of the nano-coating surface has been determined by measuring the contact angle (WCA) of the liquid drop over the solid surface through a contact angle meter optical tensiometer. For super-hydrophobic and super-hydrophilic surfaces, the WCA has been obtained to be greater than 150° and less than 5° , respectively (Figure 9).

Self-cleaning materials have been developed on the basis of that WCA less than 5° through layer-by-layer assembly of $\text{TiO}_2\text{-WO}_3$ core-shell nano-structure deposited on quartz glass slides and photo-catalytic activities of the nano-coating have been studied in terms of their ability to degrade pollutant (methylene blue)[19].

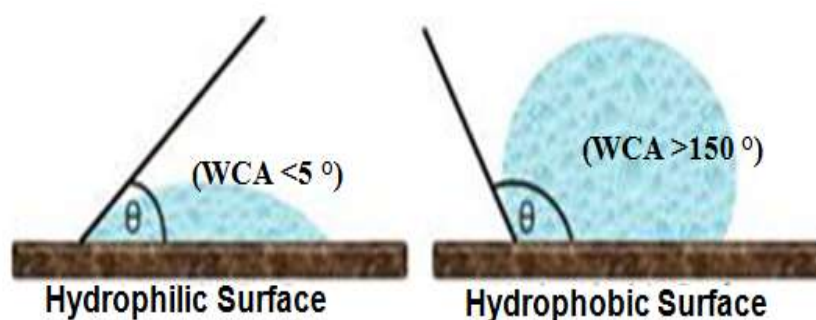


Figure 9: Contact Angle (WCA) Illustration of a Liquid Drop on a Hydrophilic and Ahydrophobic Surface

M. Akter and his co-workers [18] have investigated stain-release and ultra-violet protection properties on cotton fabric by depositing spherical ZnO nano-particles on the fabric surface. It has been reported that blue dye colour-staining on fabrics with 2.0% ZnO NPs coating has been degraded up to 78% within 24 hours under UV irradiation (Figure10a). Again, the UV protection properties of the same fabrics with 2.0% ZnONPs coating have been measured through monitoring of the transmittance value. It has been estimated that nano-coated fabric shown excellent UV-protection even up to 96% UV blockage appeared as the ultra-violet rays do not pass through the fabric surface with 2.0% ZnO NPs coating (Figure10b). In these ways, photo-catalysis technology provides us UV-protective, heat-resistant fire-fighter's suits, coffee-red wine stains-resistant garments etc.

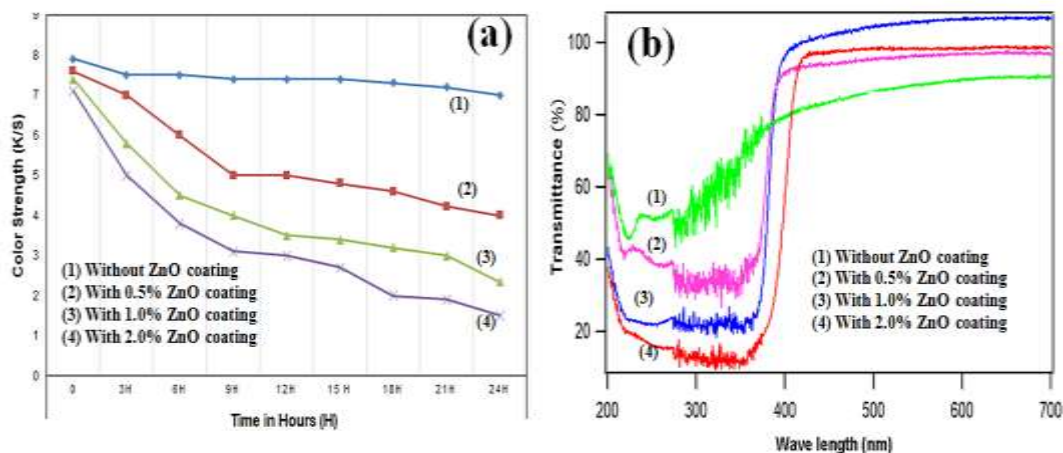


Figure 10: (A) Blue Dye Colour-Stain Degradation on Fabrics with ZnO Coating at Different Intervals of Time, (B) UV-Transmittance Curve of ZnO Non-Coating Fabric and ZnO Coating Fabric (M. Akter, 2022)

II. CONCLUSION

This chapter aims to give an overview on different photo-catalysis application in daily life based on metal chalcogenide nano-particles. These nano-particles establish an important area of research in materials chemistry that is experiencing vast growth in recent years for the sake of society. The proposed metal chalcogenide nano-particles have been widely explored as an efficient photo-catalyst for the degradation of various organic pollutants under solar and visible light illumination. The possible photo-catalytic decomposition mechanism has been discussed through the detection of reactive oxygen species (ROS) such as hydroxyl radical ($\text{OH}\cdot$), superoxide radicals ($\text{O}_2^{\cdot-}$), hydrogen peroxide radical ($\cdot\text{OOH}$). These nano-particles have also been investigated as photo-catalytic self-cleaning materials in many applications including anti-bacterial, anti-fogging, anti-reflective coatings and can provide a solution to the growing problem of environmental pollution. The proposed nano-particles have been successfully commercialized for the sake of society based on their efficiencies and availability in other different fields such as hydrogen-fuel generation as alternative energy source from water splitting, self-cleaning air purification etc. Finally, environmentally friendly, cost-effective technologies have been developed for solar-light-driven photo-catalysis so that most of the solar spectrum and light energies can be utilized in our society for large-scale application.

III. ACKNOWLEDGEMENTS

The Author is grateful to Prof. Bibhotosh Adhikary, Department of Chemistry, Indian Institute of Engineering Science and Technology (IEST), Shibpur, for helpful discussions. The Author is indebted to UGC, India for financial support through the MRP [PSW-066/15-16 (ERO)]. The author also acknowledges the MHRD (India) and UGC-SAP (India) for providing instrumental facilities to the Department of Chemistry, IEST Shibpur and RUSA Scheme of Ministry of such Education, Government of West Bengal for providing instrumental facilities to the Department of Chemistry, Bangabasi Morning College, Kolkata.

REFERENCES

- [1] R. Ameta, M. S. Solanki, S. B., S. C. Ameta, Chapter 6 - Photocatalysis, Advanced Oxidation Processes for Waste Water Treatment, Academic Press, 2018, Pages 135-175, <https://doi.org/10.1016/B978-0-12-810499-6.00006-1>.
- [2] A. K. Dutta, S. K. Maji, D. N. Srivastava, A. Mondal, P. Biswas, P. Paul, B. Adhikary. Synthesis of FeS and FeSe Nanoparticles from a Single Source Precursor: A Study of Their Photocatalytic Activity, Peroxidase-Like Behavior, and Electrochemical Sensing of H₂O₂. ACS Appl. Mater. Interfaces, 2012, 4(4), pp 1919–1927.
- [3] A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, Nature, 1972, 238, pp 37–38.
- [4] A. K. Dutta, S. K. Maji, B. Adhikary, γ -Fe₂O₃ nanoparticles: An easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant, Mater. Res. Bull., 2014, 49, pp 28–34.
- [5] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahemann, Environmental Applications of Semiconductor Photocatalysis, Chem. Rev., 1995, 95 (1), pp 69–96.
- [6] T. Mano, Water treatment efficacy of various metal oxide semiconductors for photocatalytic ozonation under UV and visible light irradiation, Chemical Engineering Journal, 2015, 264, pp 221–229.
- [7] K. Nakata, A. Fujishima, TiO₂ photocatalysis: Design and applications, J. Photochem. Photobiol. C Photochem. Rev., 2012, 13, pp 169–189.
- [8] M. Sun, D. Li, W. Li, Y. Chen, Z. Chen, Y. He, X. Fu, New Photocatalyst, Sb₂S₃, for Degradation of Methyl Orange under Visible-Light Irradiation, J. Phys. Chem. C, 2008, 112 (46), pp 18076–18081.
- [9] A. Sarkar, A. B. Ghosh, N. Saha, A. K. Dutta, D. N. Srivastava, P. Paul, B. Adhikary, Enhanced photocatalytic activity of Eu-doped Bi₂S₃ nanoflowers for degradation of organic pollutants under visible light illumination, Catal. Sci. Technol., 2015, 5, pp 4055–4063.
- [10] H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M. A. Fox, R. B. Draper, Kinetic studies in heterogeneous photocatalysis. Titania-mediated degradation of 4-chlorophenol in air-equilibrated aqueous media, Langmuir, 1989, 5(1), pp 250-255.
- [11] J. C. Barreto, G. S. Smith, N. H. P. Strobel, P. A. McQuillin, T. A. Miller, Terephthalic acid: a dosimeter for the detection of hydroxyl radicals in vitro, Life Sci., 1995, 56(4), pp 89–96.
- [12] M. Shen, M. A. Henderson, Identification of the Active Species in Photochemical Hole Scavenging Reactions of Methanol on TiO₂, J. Phys. Chem. Lett. 2011, 2 (21), pp 2707-2710.
- [13] R. Banerjee, A. Pal, D. Ghosh, A. B. Ghosh, M. Nandi, P. Biswas, Improved photocurrent response, photostability and photocatalytic hydrogen generation ability of CdS nanoparticles in presence of mesoporous carbon, Mater. Res. Bull., 2021, Volume 134, pp 111085.
- [14] A. K. Dutta, Photo-catalytic degradation of methylene blue dye using Fe₃O₄ nanoparticles in the waste-water treatment plant” unpublished
- [15] J. Zhao, X. Yang, Photocatalytic oxidation for indoor air purification: a literature review, Building and Environment, 2003, Volume 38, Issue 5, Pp 645-654.
- [16] Y. H. Li, S. H. Yang, C. S. Yuan, H. Shen, C. H. Hung, Photocatalytic Degradation of Gaseous Acetone by Photocatalysts with Visible Light and their Potential Applications in Painting, Aerosol Air Qual. Res., 2023, 23, pp 220358.
- [17] T. S. Nagarjunan, J. G. Calvert, J. Phys. Chem., 1964, 68(1), pp 17-26.
- [18] I. S. Tania, M. Ali, M. Akter, Fabrication, characterization, and utilization of ZnO nanoparticles for stain release, bacterial resistance, and UV protection on cotton fabric, Journal of Engineered Fibers and Fabrics, 2022, pp 17.
- [19] A. O. T. Patrocinio, L. F. Paula, R. M. Paniago, J. Freitag, D. W. Bahnemann, ACS Appl. Mater. Interfaces, 2014, 6, pp 16859-16866.