Metal Chalcogenide Nano-particles based multiple photo-catalysis in daily life

Dr. Amit Kumar Dutta

Department of Chemistry, Bangabasi Morning College, 19, Rajkumar Chakraborty Sarani, Kolkata- 700009

ABSTRACT

Development of innovative nano-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, CdS NPs etc. and their composite have been synthesized and established as effective heterogenous recyclable catalyst for conducting several photo-chemical reactions. When the nano-materials have ability to absorb solar light energy, the performance for photo-catalytic reactions has been increased much more. In this chapter it has been 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 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

I. INTRODUCTION

Photocatalysis is one of the most useful methods where photo-energy is used to conduct a chemical reaction [1]. The term ‘Photocatalysis’ 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 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, focus needs to be done on improving environmentally friendly, low-energy, 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 typically has been utilised world-wide for complete decomposition of organic pollutants in presence of a nano-catalysts material under light illumination. Very recent, photo-catalysis have 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 break down 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-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 (TiO_2) working electrode and a Platinum counter electrode, when light was fallen on the TiO_2 electrode, a 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 TiO_2 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].

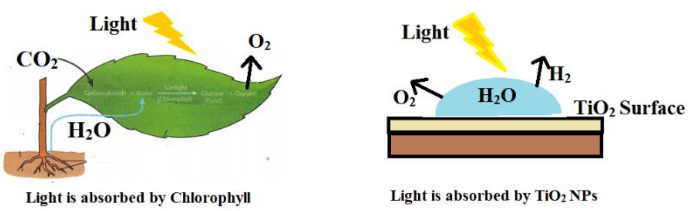


Figure 1: Photo-catalysis technology on TiO_2 surface, basically analogous to the photo-synthesis technique in plant

As a catalyst material, nano-sized inorganic materials show remarkable efficiency in the field of photo-catalysis technology. As the dimension of the nano-scaled materials so small, new interesting properties have been generated such as interesting chemical and physical properties, large specific surface area, 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 suitable band gap energies and flat band potential levels that can easily absorb light energy and accelerate the photo-chemical reaction rate [5]. Most of the metal chalcogenides nano-particles such as metal oxides, metal sulfide TiO_2, ZnO, CuO, FeS, ZnS NPs 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, 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, TiO_2-based semiconducting nano-materials are one of the most promising candidates for photo-catalysis applications, mainly due to its photo-chemical stability and high oxidation power (3.2 eV vs. NHE, which corresponds to photons with a wavelength of 388 nm), 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-titania-based materials such as CuO, ZnO, FeS, ZnS etc. and even doped hetero-nanostructures Bi_2S_3/BiOCl, Eu-doped Bi_2S_3 have been found to exhibit visible and solar-light-driven catalytic activity [8,9].

Keeping in mind the multiple photo-catalytic application 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 possible mechanism of the photo-catalytic 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 decomposition and remediation of organic pollutants in waste-water treatment, 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 detailed information on a photo-catalysis based number of 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 suitable band gap and flat band potential levels with filled valance band (VB) and vacant conduction band (CB) (Figure 2). Titanium dioxide (TiO_2) nano-material has been chosen as the model material for basic investigation and to demonstrate general surface photocatalytic reactions of semiconductors. It is generally accepted that the main reaction responsible for photocatalysis is the interfacial redox reaction 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 VB will absorb the photon and be promoted to the CB, thus leaving behind hole in VB 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 (O_2) and hole can abstract electron from water bodies to generate hydroxyl radical (OH•) and other reactive oxygen species (ROS) [10]. These radicals actually convey the photo-chemical reactions.

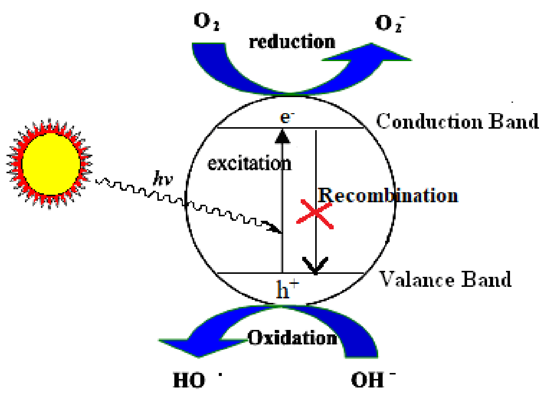


Figure 2: Illustration of photo-catalytic mechanism

The overall reactions are presented in following equations.

$$TiO_2 + h\nu \longrightarrow TiO_2 \;(e^-_{CB} + h^+_{VB})$$

$$H_2O \longrightarrow H^+ + OH^-$$

$$OH^- + h^+_{VB} \longrightarrow OH^{\cdot}$$

$$\text{Pollutants} + OH^{\cdot} \longrightarrow \text{Products}$$

The aromatic dyes have been further degraded by O_2^- active species and superoxide radicals (O_2^{-}•), which was generated on the surface of the proposed NPs according to following equations.

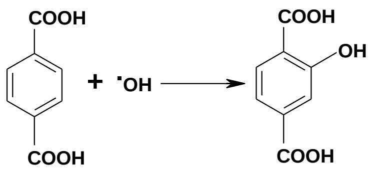
$$O_2 + e \longrightarrow O_2^-$$

$$O_2^- + 2\,H^+ + 2e \longrightarrow H_2O_2$$

$$H_2O_2 + e \longrightarrow OH^- + {}^{\cdot}OH$$

$$\text{Pollutants} + OH^{\cdot} \longrightarrow \text{Products}$$

As a whole, both O_2^- and OH• are responsible for photo-chemical reactions.
The formation of OH· has been confirmed by terephthalic acid (TA) photoluminescence probing, which is usually used in detection of hydroxyl 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· and is converted to highly fluorescent 2–hydroxy terephthalic acid (HTA) according to following equation.



(TA) (HTA)

If that band gap energy becomes tremendous low, the lifetime of the produced electrons and holes in its surface becomes low, there is a possibility of the recombination of electron–hole pairs and hence the photocatalytic activity is decreased. In that case, doping with metals, non-metals, formation of hetero-junctions between TiO_2 and other low bandgap semiconductor and fabrication of graphene-based semiconductor nano-composited can suppress the recombination of electron–hole pairs, enhance their lifetime and improve activity of doped TiO_2 photocatalyst (Figure 2). In hetero-nanostructure, lattice mismatch arises in the 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, thereby 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 have been widely applied for hydrogen-fuel production as alternative non-carbon energy source. This is the low-cost method and not evaluate harmful CO_2 gas, like natural fossil fuels (coal, oil, natural gas etc.), which makes serious impact on our environment be 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 photocatalyst under light illumination and mild conditions according to equation

$$2\,H_2O + 4\,h^+ \rightarrow 4\,H^+ + O_2 \;(E^0 = 1.23 \text{ V vs. RHE})$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \;(E^0 = 0 \text{ V vs. RHE})$$

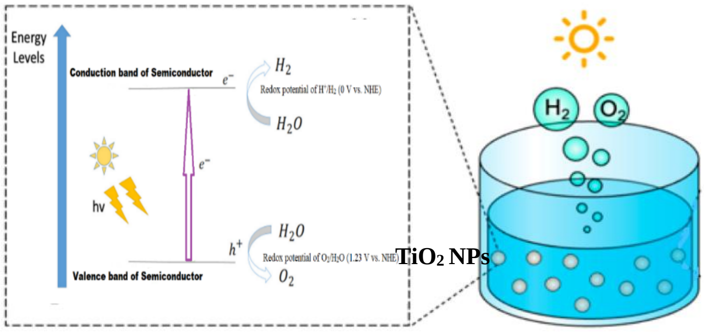


Figure 3: General illustration for water splitting on TiO_2 nano-catalyst

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 transfer to the active sites of the surface of semiconductor photocatalyst, they will act as reducing/oxidizing agents to drive reduction/oxidation reaction on the surface. In water splitting process, water molecules are reduced by the photo-induced electrons to form H_2 and are oxidized by the photo-induced holes to form O_2 i.e., the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) (Figure 3). The hydrogen gas produced was collected using gas-tight syringe and analysed by gas chromatography.

From the thermodynamic restrictions, a semiconductor photocatalyst that has the ability to split water to produce hydrogen must have a flat band positions in such a way that the bottom level of the conduction band (CB) position should be more negative than the redox potential of H^+/H_2 (0 V vs. NHE) for evolution of hydrogen and the top level of the valences band (VB) 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 photocatalyst for water splitting process is 1.23 eV. Figure 4 Represents the band potential positions of several metal chalcogenide semiconductor relative to the water redox potential levels which can efficiently split water to produce hydrogen. For TiO_2, its band gap is large enough to split water (3.0 eV vs. 1.23 eV for the formation of H_2 and O_2) and also its band structure matches well with redox potentials of water splitting.

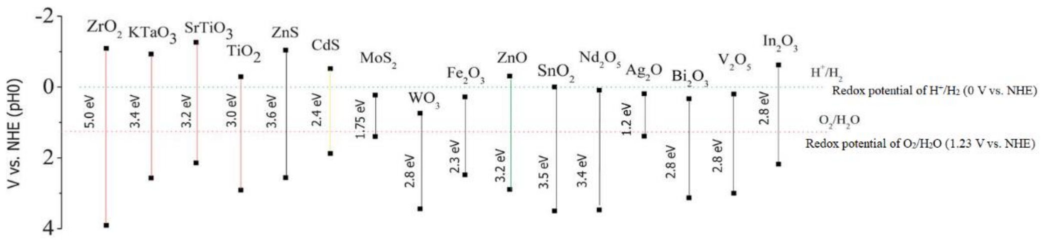


Figure 4: Band potential position of several metal chalcogenide semiconductors against normal hydrogen electrode (NHE) as a reference

Though fulfilling thermodynamic potential level condition, some nano-materials cannot efficiently produce hydrogen because the photo-generated electrons and holes that can migrate to the photocatalyst surface will reduce protons to form H_2. It has been seen that most of the photo-generated electrons and holes can recombine on the photocatalyst 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 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 his co-workers [13], the rate of H_2 production from water over a heterogeneous photocatalyst, CdS-carbon nano-composite (40 MC/CdS of Figure 5), has been found to be much higher ie 37,641 μmol/g/h due to presence of suitable flat band potential and photo-generated charge separation ability of catalyst.

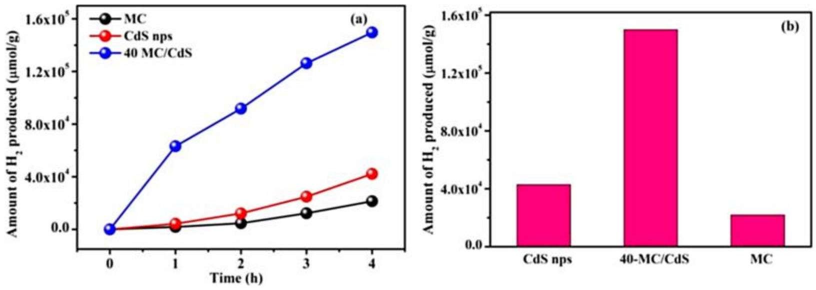


Figure 4: (a) Photo-catalytic hydrogen-fuel production (µmol/g/h) in presence of different CdS NPs (b) comparative study of H_2 production obtained after 4 h of light irradiation (R. Banerjee, 2021).

3. Photo-catalytic decomposition and remediation of organic pollutants in waste-water treatment

In the waste-water treatment, photo-catalytic activity of the proposed nano-scaled materials have been tested through degradation 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 550–750 nm under visible light illumination. The UV–vis absorption curves decrease rapidly with the irradiation time (Figure 5A) catalysed by Fe_3O_4 NPs and the corresponding solution became colourless (Figure 5A inset) within few hours "unpublished" [14]. A comparative performance has been illustrated in Figure 5B with Fe_3O_4 NPs and commercial TiO_2, where it has been shown that the degradation of MB has been achieved up to 99% within few hours and the corresponding solution became colourless. 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.

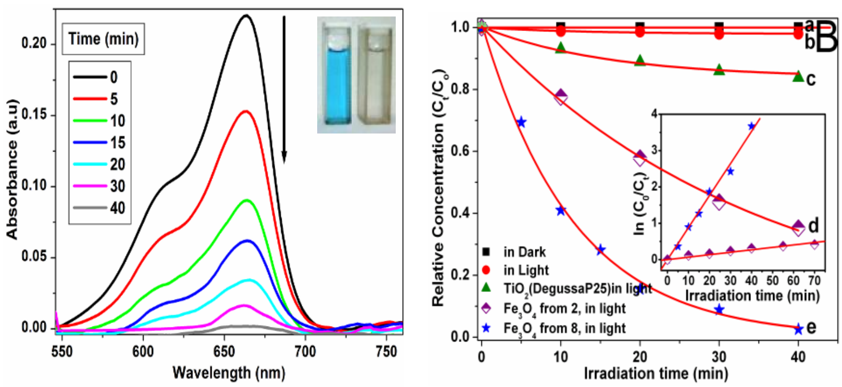


Figure 5: (A) UV–Vis spectral changes of MB in aqueous Fe_3O_4 dispersion as a function of irradiation time. Insets show the photography of corresponding colour change during degradation process, (B) Corresponding reaction profile with pseudo–first order kinetics fitting.

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 fllowing equation

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

where C_0 represents the initial concentration, C_t denotes the concentration at a given reaction time '*t*', and *k* is the 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

Table 1: Comparison of the kinetic parameters for the photo-catalytic activity of the proposed nano-scaled semiconductor nanomaterials.

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 P-25)	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 a 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, nitrogen oxides, 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 materials' emission, the combustion processes as well as the use of household 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 (OH.) superoxide radicals (O_2^{-}•) hydrogen peroxide radical (•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 pollutants molecules break-down into harmless Substances CO_2 and H_2O. Yu-Hua Li and his co-workers [16] have investigated a photo-catalytic degradation of gaseous acetone in a Pyrex glass cylindrical batch reactor using paints made of Fe-doped TiO_2 nano-particles under light illumination and the acetone degradation efficiencies of 46.2% have been observed using the paints made of 3% Fe-doped, which could effectively control indoor acetone pollution.

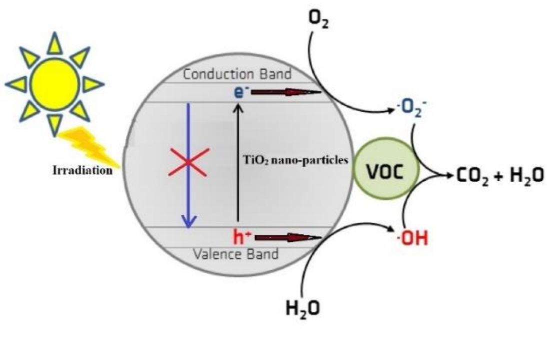


Figure 6: Illustration of photo-catalytic oxidation (PCO) technology of VOCs

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 CO_2 or CO_3^- is necessary. Though The oxidation of gas phase CO into CO_2 is a thermodynamically favourable, but it requires high energy barrier ie. 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

$$\mathrm{ZnO} + h\nu \rightarrow h^+(\mathrm{ZnO}) + e^-(\mathrm{ZnO})$$

$$h^+(\mathrm{ZnO}) + \mathrm{CO} \rightarrow \mathrm{CO}^+(\mathrm{ZnO}),$$

$$\mathrm{O_2(ZnO)} + e^-(\mathrm{ZnO}) \rightarrow \mathrm{O_2^-(ZnO)},$$

$$\mathrm{O_2^-(ZnO)} + \mathrm{CO^+(ZnO)} \rightarrow \mathrm{CO_3(ZnO)},$$

$$\mathrm{CO(ZnO)} + \mathrm{CO_3(ZnO)} \rightarrow \mathrm{2CO_2(ZnO)},$$

$$\mathrm{O_2^-(ZnO)} + e^-(\mathrm{ZnO}) \rightarrow \mathrm{2O^-(ZnO)},$$

$$\mathrm{O^-(ZnO)} + \mathrm{CO^+(ZnO)} \rightarrow \mathrm{CO_2(ZnO)},$$

$$\mathrm{CO_3(ZnO)} + e^-(\mathrm{ZnO}) \rightarrow \mathrm{CO_3^-(ZnO)},$$

$$\mathrm{CO_3^-(ZnO)} + \mathrm{CO^+(ZnO)} \rightarrow \mathrm{2CO_2(ZnO)},$$

During purification from H_2S or SO_x, Sulphur has been converted to sulfurtrioxide (SO_3) or sulfate (SO_4^{2-}) 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-exited electron and valence band hole (h^+_{VB}) on the nano-catalyst surface can generate reactive oxygen species (ROS) that can convert dirt organic matter into CO_2 and water resulting in the cleaning of the surface.

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 nanoparticle coated textiles and clothing. TiO_2, ZnO, type semiconducting materials have ability to absorb ultraviolet radiation and can protect the textile fabric from the harmful effect of UV rays. Also, our body gets protection by wearing sun-protective clothes made of semiconducting nanoparticle coated textile fibres. Additionally, when exposed to ultraviolet light, the photo-catalytic characteristic of the semiconducting nanoparticle allows it to act as self-cleaning agent by photo-catalytic degradation of various colour stains. Even, photo-catalytic self-cleaning ability have been retained after several cycles of home-washing. Thus, photo-catalysis technology provides UV-protective, heat-resistant fire-fighter's suits, coffee-red wine stains-resistant garments etc.

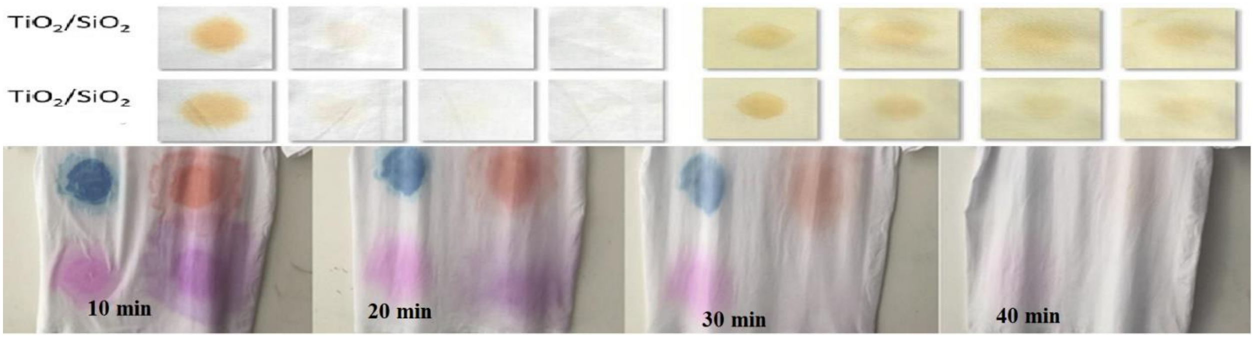


Figure 7: Self-cleaning observation of fabrics with TiO_2/SiO_2 coating under light irradiation

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.

M. Akter and his co-workers [18] have investigated stain-release and UV (ultra-violet) protection properties on cotton fabric by depositing spherical ZnO nanoparticles (average size of 40–100 nm) on the fabric surface. It has been reported that blue dye colour-staining on fabrics with 2% ZnO coating has been degraded up to 78% within 24 h under UV irradiation (Figure). Again, the UV protection properties of the same fabrics with 2% ZnO coating has 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 UV rays do not pass through the fabric surface with 2% ZnO coating.

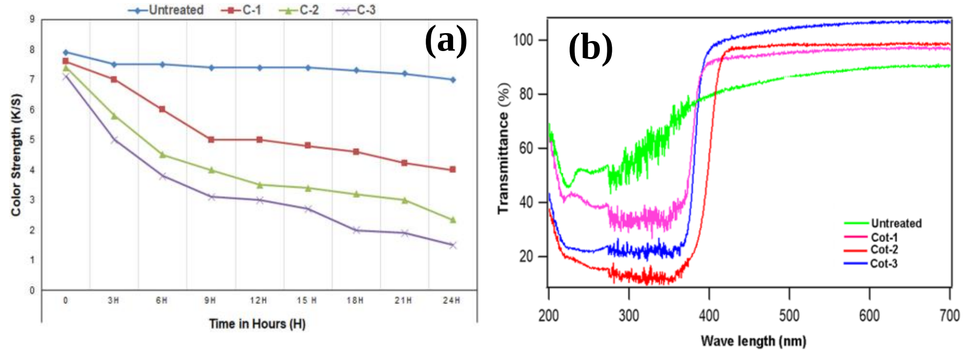


Figure 8: (a) Blue dye colour-stain degradation on fabrics with ZnO coating at different intervals of time, (b) UV transmittance curve of fabric with ZnO non-coating and with ZnO coating (M. Akter, 2022)

The self-cleaning efficiency of the nano-catalyst materials also depends the basic surface properties, 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. 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 have been determined by measuring the contact angle (WCA) of the liquid drop over the solid surface through a contact angle meter optical tensiometer, where 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 TiO_2-WO_3 core-shell nano-structure deposited on quartz glass slides and photo-catalytic activities of the nano-coating have been examined in terms of their ability to degrade methylene blue dye [19].

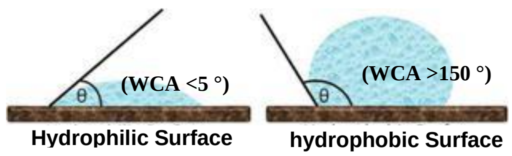


Figure 9: Contact angle (WCA) representation of a liquid drop on a hydrophilic and a hydrophobic surface

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-materials constitute an important area of research in materials chemistry that is experiencing vast growth in recent years for the sake of society. the proposed nano-scaled materials 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 also been discussed through the detection of detection of reactive oxygen species (ROS) such as hydroxyl radical (OH•), superoxide radicals (O_2^{-}•) hydrogen peroxide radical (•OOH). These photo-catalytic self-cleaning materials can also be used 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-materials have been successfully commercialized for the sake of society based on their efficiencies and availability in other different field such as hydrogen-fuel generation as alternative energy source from water splitting, self-cleaning air purification etc. The catalytic performances have also been improved by tuning band-gap energy and surface area during synthesis process. Finally, an 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.

I. *Acknowledgements*

The Author is grateful to Prof. Bibhutosh Adhikary, Department of Chemistry, Indian Institute of Engineering Science and Technology (IIEST), 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, IIEST Shibpur.

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, pp37–38.

[4] A. K. Dutta, S. K. Maji, B.Adhikary, γ–Fe_2O_3 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, pp28–34.

[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, pp221–229.

[7] K. Nakata, A. Fujishima, TiO_2 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 Fe_3O_4 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.