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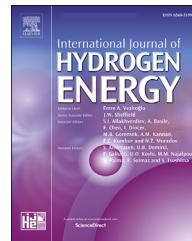


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Photocatalytic semiconductor thin films for hydrogen production and environmental applications

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ABSTRACT

The semiconducting thin film materials are the main key elements in the fields of photonic, electronic and magnetic devices. The preparation of materials in the form of thin films allows easy incorporation into various through changing the properties of materials and reducing the size. The core benefits of thin film systems are cost reduction and efficiency of devices. They are widely used for the protection of surfaces, chemical resistance and to modify electrical and optical properties. The study on semiconducting thin films is rapidly growing due to their constructive applications in wireless communication, solar cells, semiconductor devices, integrated circuits, magneto-optic memories, light emitting diodes, multifunctional protective coatings, liquid crystal displays, and so on. This review explains about recent achievements in the photocatalytic nanostructured semiconducting thin films, their deposition, fabrication methodologies, controlling of film micro/nanostructures, physicochemical properties, photocatalytic mechanism and its photocatalytic applications in the fields of energy such as hydrogen generation, CO₂ reduction to useful chemicals, and environmental remediation such as photodegradation of harmful bacteria and toxic chemicals.

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Introduction

It is not an overstated fact that the low dimensional materials are likely redefining the materials properties at nanoscale [1].

Thin films are in this direction made a revolutionary impact in the technological developments of various fields ranging from health care, energy, and environmental applications [2–4]. Thin films are generally defined as two-dimensional (2D) materials with thickness ranging from nanometer to

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micrometer [5,6]. 2D materials essentially represent the quantum confinement of electrons along one direction and unfettered movement of electrons along other two directions in the materials [7]. The combinations of these fettered and unfettered dimensions will possibly lead to the synergistic effect of both bulk and nano-properties in the materials. Apart from the dimension induced features and functions, the structural flexibility of thin films is greatly beneficial to the device materials for their applications [8]. For instance, thin films are largely used to develop electronic displays, smart windows, sensors, and so on as shown in Fig. 1. Unlike the deposition of materials onto the substrates in bulk forms, thin films are generally atomically arranged materials that can be directly applied to construct the device with necessary built-in auxiliaries.

Thin films are a reliable and potential way of structuring the materials. It has gained technological importance as it helps miniaturizing the devices [9]. The confinement of electric charges due to their fettered dimensions leads to sensitize the materials at the interfaces, where it drives the properties of the material to a greater extent. This is the reason that in recent times, the exploration of the physics of materials structure has been given importance in materials developments [10]. As a result, these confined structures opened up the new challenges towards their synthesis, characterizations, and modeling for various applications. Structures in terms of size and morphology of the materials play paramount importance in achieving the materials with desired properties towards the designated applications [11]. In the current scenario, the need for materials with tunable properties and flexible device construction is highly crucial in the field of energy and environment. Among the few techniques in addressing the energy and environmental issues, photocatalysis holds a unique place due to their versatile properties and process, which can be reliable and flexible towards industrial scale applications [12].

Photocatalysis is the process of light-induced redox reactions upon the surrounding molecules to produce radical species for the subsequent utilization in the water splitting for H₂ and O₂ production, various pollutant degradations, CO₂ conversion into hydrocarbon fuels, disinfection of microorganism, etc [13] as shown in Fig. 2. A process such as photocatalysis, which can be manifested for diverse applications, is

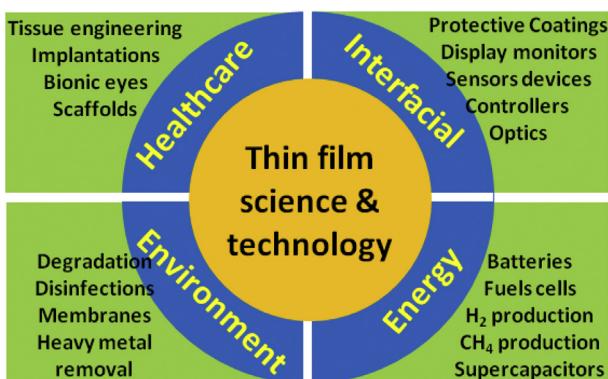


Fig. 1 – Various applications of thin film science and technology.



Fig. 2 – Applications of photocatalytic process. Reprinted with permission from Ref. [19].

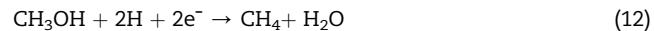
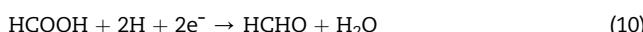
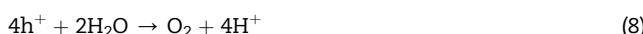
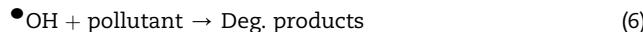
ideal for large scale applications in real time. With such advantages, the careful selection or engineering of materials and structures for photocatalysis, i.e. photocatalysts are important as to efficiently perform the photocatalytic reactions. An ideal photocatalyst bound to possess (i) narrow band gap energy, (ii) suitable band edge potential, (iii) reduced recombination, (iv) enhanced charge separation and (v) improved charge transports [14]. As to achieve this, photocatalytic materials are modified for their chemical compositions and physical structures. The former can be done through doping [15], composite formation [16], metal sensitization, molecule functionalizations [17], etc. Similarly, the latter includes the size, shape and surface morphology modifications of the materials. In this context, thin films are essentially the physical structure modification of materials, where the desired photocatalytic materials will be grown into thin films through the bottom-up process by depositing molecular phase of the materials onto a substrate to grow into a solid material. Later, the deposited thin films can be used along with the substrate or peeled off and utilized as free-standing thin films. On the other hand, reactor designs for photocatalytic applications play an important part in industrial scale implementation [18]. Thin films have the potential to be employed in the industrial scale as it simplifies the handling of photocatalytic materials in several aspects such as their convenient design that adaptable in the reactors, recyclability, recovery, etc. Therefore, the meticulous design of photocatalytic thin films would be ideal for their large scale applications.

This review has been constructed to provide insights into the development of thin films towards various photocatalytic applications. Accordingly, firstly it outlines the photocatalytic mechanisms in thin film materials, various methods for the fabrication of thin films, characterization techniques and applications such as pollutant degradations, H₂ production, CO₂ conversion into hydrocarbon fuels, antibacterial disinfection

and so on. Finally, it concludes with the future directions in thin film technology towards photocatalytic applications.

Mechanism of photocatalytic process

In the photocatalytic process, the light irradiation on the semiconductor photocatalysts causes the excitation of electrons to the conduction band (CB) and the creation of holes in the valence band (VB). Subsequently, these electrons and holes involve in the reduction and oxidation reactions, respectively over the water molecules and produce super oxide anions and hydroxyl radicals, respectively [20]. Then these radical species further involved in the degradation and other processes, which is generally known as the photocatalytic process as shown in Fig. 3(a). For instance, the typical photocatalytic process towards pollutant degradation (eqns [1–6]), water splitting (eqns [7–8]) and CO₂ conversion into CH₄ (eqns [9–12]) can be described as follows.



The essential characteristics of structuring the photocatalytic materials in the form of thin films involve the changes in the band structure of materials that energetically favor the above-listed reactions through the appropriate positioning of band edge potentials in the thin film photocatalyst [21]. For instance, Fig. 3(b) shows the different possible CB and VB edge positions that support the redox reactions in a photocatalyst. It reveals that the overall water splitting will take place only if the CB and VB are positioned to be more positive and negative, respectively on the NHE scale [22]. For example, Fig. 4(a) shows the optical properties of Cd(O, S) thin films fabricated using magnetron sputtering technique, in which the mere introduction/control over oxygen gas during the sputtering process led to the thin films optically transparent [23]. Similarly, Fig. 4(b) shows the changes in the band gap energy of ZnO thin films that merely tuned by increasing the oxidation temperature [24]. Therefore, the design of photocatalyst with such tunable optical properties is largely possible in thin film structures, where it can be implemented through controlling the experimental parameters during the thin film fabrication (see Fig. 5).

Preparation of thin films

The following is a classification of thin films and selected important literature references for deposition of thin-films are in Table 1. Thin films with good quality can be obtained by two techniques: chemical and physical depositions. Additionally, thin films consist of a layer and the substrate where the films are deposited on it. Also, thin films may be consists of multiple layers such as electrochromic cells, thin-film solar cells and so on.

Evaporation methods

Evaporation method one of the oldest techniques used for depositing thin films and still widely used in the industry and laboratory for deposition of semiconductor materials and

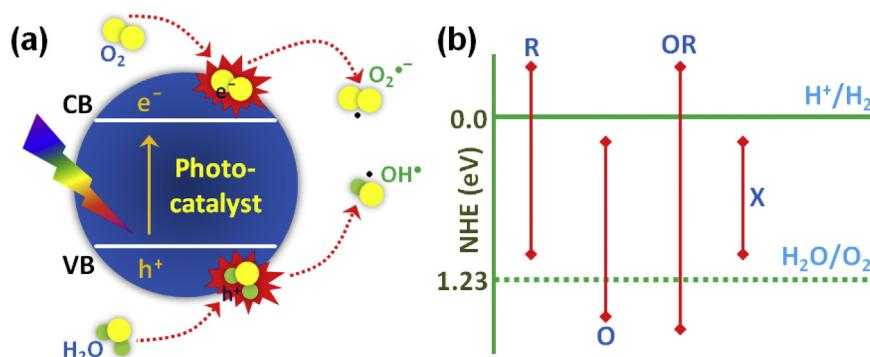


Fig. 3 – (a) Photocatalytic process in semiconductor, and (b) band edge potential and respective redox reactions R-Reduction, O-Oxidation, OR-Reduction & Oxidation and X-No reaction.

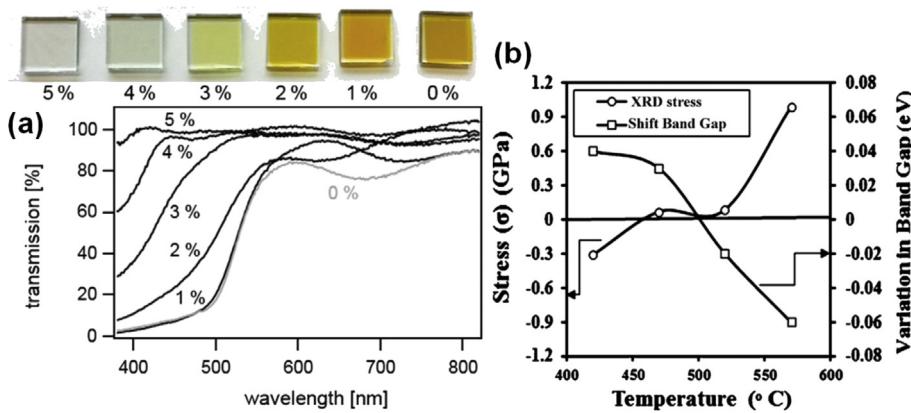
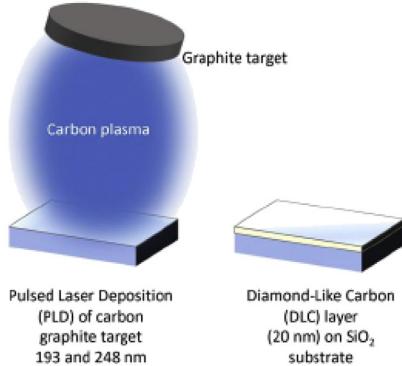


Fig. 4 – (a) Deposition of Cd(O, S) films through reactive magnetron sputtering with a change in amount of oxygen: (top) pictorial images, (bottom) transmission spectra, and (b) Variation in band gap and stress in the ZnO thin films with wet oxidation temperature.

STEP 1 : Laser Deposition



STEP 2 : Laser Annealing

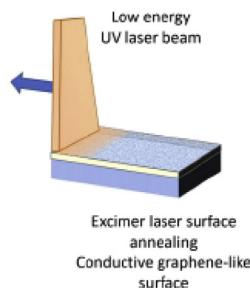


Fig. 5 – Schematic of PLD technique. Reprinted with permission from Ref. [36].

among all thermal evaporation or vacuum evaporation is extensively using method. The general mechanism of this method involves changing the phase of the material from solid to vapor phase and converting back to a solid phase on the specific substrate under vacuum or controlled atmospheric condition.

Table 1 – Different methods of thin films deposition techniques [25].

Physical deposition	Chemical deposition
1. Evaporation techniques	1. Sol-gel technique
a. Vacuum thermal evaporation.	2. Chemical bath deposition
b. Electron beam evaporation.	3. Spray pyrolysis technique
c. Laser beam evaporation.	4. Plating
d. Arc evaporation.	a. Electroplating technique.
e. Molecular beam epitaxy.	b. Electroless deposition.
f. Ion plating evaporation.	5. Chemical vapor deposition (CVD)
2. Sputtering techniques	a. Low pressure (LPCVD)
a. Direct current sputtering (DC sputtering)	b. Plasma enhanced (PECVD)
b. Radio frequency sputtering (RF sputtering)	c. Atomic layer deposition (ALD)

Vacuum evaporation

Vacuum evaporation technique is the simplest technique to deposit amorphous thin films specially chalcogenide films such as MnS [26], CdSSe [27], Ge-Te-Ga [28], and many more on various substrates. The process involves thermal vaporizing of the material followed by condensing back to the solid state on the substrate, Klenk et al., demonstrated the deposition of CuInSe₂ polycrystalline thin film which follows the Boeing recipe for the fabrication of solar cell. Typically, the bottom layer was deposited by evaporating Cu and Se precursor. The substrate temperature was kept constant at 490 °C, whereas the In was injected through the liquid phase and mechanism is based on the presence of low-temperature Cu-Se phase and also growth is aided by liquid phase In and Se dissolved in liquid phase [29].

Electron beam evaporation

(EBV) is a physical technique. An electron beam is generated from the filament is transfer through electric and magnetic fields and hit the target and finally strike the target followed by vaporizing it under a vacuum environment. Different materials such as amorphous and crystalline semiconductors

[30], metals [31], oxides [32], and molecular materials [33] are prepared by EBV technique. The typically ZnO thin films were deposited on the quartz substrate by using an electron beam evaporation technique using 4N-ZnO pellets. Subsequently, deposition temperature varied from 200C to 400C [34]. After deposition, the films were annealed at 500, 600 and 800 °C for 1 h.

Laser beam evaporation (pulsed-laser deposition)

PLD involves vaporizing a material using a laser beam like KrF (248 nm), and XeCl (308 nm) for deposition on thin films inside a vacuum chamber. The quality of thin-film depends on the diverse parameters such as the wavelength of the laser, energy, ambient gas pressure, pulsed duration, substrate temperature and the distance of the target to the substrate [35]. PLD has the advantage of fast deposition time and compatibility to oxygen and other inert gases. Stock et al., demonstrated the deposition of diamond-like carbon using PLD technique. The laser was focused on the surface of the pure graphitic source in a high vacuum. When the laser bombards the target, the material is ablated perpendicularly to the surface and collect on the substrate set parallel to it. The layer is mainly deposited mainly on the Silicon substrate [36].

Sputtering technique

Sputtering is the most basic and well-known technique where the atoms are evaporated (ejected) on to a substrate material surface through bombarding with high energetic particles under high temperature and vacuum [37].

Two classes of the sputtering process, a) direct current (DC) process using target materials with electrical conductivity b) radio frequency (RF) sputtering uses radio frequency power for most dielectric materials. An example of DC and RF sputtering is aluminum nitride films [38] (see Fig. 6)

Chemical deposition techniques

Thin films deposition from physical methods is expensive and require a large amount of target although gives good quality thin films. Chemical deposition techniques are widely used

and cost-effective methods to produce high-quality thin films. The film deposition depends on pH value, solution chemistry, and viscosity. The general chemical deposition processes are chemical vapor deposition (CVD), electrodeposition, sol-gel, spray pyrolysis technique and chemical bath deposition. This segment explains chemical bath deposition and sol-gel methods of deposition [25].

Sol-gel technique

It is one of the famous wet-chemical methods and widely used for the synthesis of transition metal oxide [39]. It requires lesser-temperature and provides improved homogeneity for multi-component materials. The process involves the construction of a colloidal suspension and converting to viscous gels or solid materials. This method involves alkoxides where the hydrolysis of alkoxy group results in macromolecular oxide network followed by polycondensation reactions takes place.

Deposition of thin films from sol can be achieved by the following methods:

- (i) Dip coating
- (ii) Spin Coating
- (iii) Spraying

Dip-coating process. Dip-coating is an old commercially applied thin film deposition method. It involves controlled immersion of the substrate into a sol to be coated followed by withdrawal, which gives a uniform thickness of up to 1 μm [40].

Spin-coating technique. The spin coating involves the deposition of thin films on substrates, where the substrates spin perpendicular to the coating area. The advantage of spin coating is fast and easy to produce very uniform films, ranging from nanometers to microns thickness [41].

Chemical bath deposition technique

Thin films deposition from physical methods is expensive and require a large amount of target although produces enhanced quality thin films. Chemical deposition techniques are widely used and cost-effective methods to produce high-quality thin films. The film deposition depends on pH value, solution chemistry, and viscosity. The general chemical deposition processes are chemical vapor deposition (CVD), electrodeposition, sol-gel, spray pyrolysis technique and chemical bath deposition. This segment explains chemical bath deposition and sol-gel methods of deposition [42].

Electrochemical synthesis

The electrochemical synthesis of thin films is a cost-effective method because it doesn't require expensive instrumentation to form thin films with large surface area to volume ratios. Zhu et al. have reviewed the synthesis and photoelectrocatalytic water oxidation of WO₃ thin films. WO₃ thin films were widely synthesized with electrochemical syntheses like electrochemical anodization and cathodic electrodeposition. Electrochemical anodization is carried out by

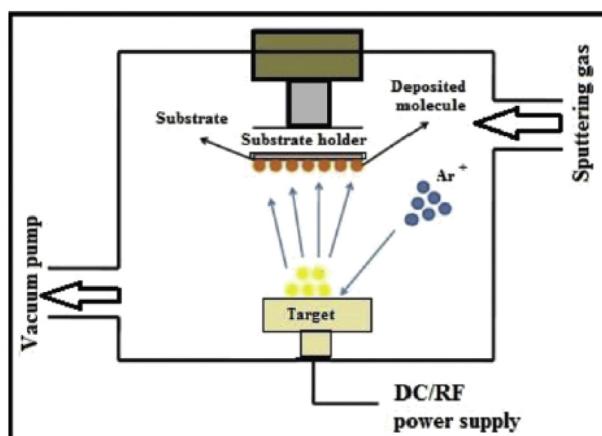
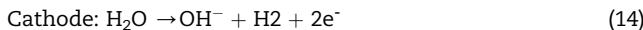
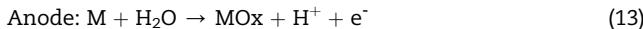


Fig. 6 – The image of sputtering system. Reprinted with permission from Ref. [38].

applying potentials and/or current densities and the metal is used as the anode [43]. Eqs. (1) and (2) show the half reactions that occur in a PEC cell set up at both the anode and cathode.



Where M corresponds to the metal. Equation (1) shows the WO_3 layer growth and at the cathode, H_2 evolution occurs as per Eq. (2). Cathodic electrodeposition involves two different mechanisms which are (a) reduction of oxidation state and deposition of the metal on the electrodes and (b) higher interfacial pH and local supersaturation leading to metal oxide precipitation. Properties of nanostructured WO_3 like size, thickness, the composition can be modified by varying the preparation condition [44].

Hydrothermal method

Hydrothermal method is one of the versatile methods for the synthesis of nanomaterials. The advantage of the hydrothermal method which uses the relatively low-temperature crystalline structures is deposited at a relatively high rate than compared to other methods. However, it is very difficult to control the chemical composition. Hence this method is less commonly used for the thin film synthesis. Shimura et al., synthesized the lead zirconate solid solution using the hydrothermal method to get the better crystallinity of the thin films [45]. The purpose of this method was to control the nucleation and growth of the material to get better crystalline material even though it was a 2 step process for obtaining a thin film. Morita et al., demonstrated that this material can be synthesized as a thin film through a single step process [46]. Urgessa et al., demonstrated the synthesis of well-defined smooth ZnO nanorod thin films through hydrothermal route. They demonstrated the nucleation and growth can well control in hydrothermal route, through changing the concentration of citric acid [47]. Researchers are working to develop a better thin film using simple hydrothermal methods.

Chemical vapor deposition (CVD)

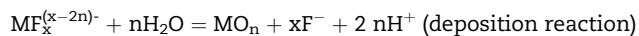
Formation of thin films via the process of chemical reactions from the gaseous phase is called CVD. The reaction or deposition is initiated or started by electric or thermal discharge plasma treatment. Some of the complexes and reducing compounds such as ammonia complexes, other halogenated compounds such as chlorides, fluorides, bromides and some of the organometallic compounds are used for initiation of activation for chemical reaction that provides a metallic component deposition. After the dissolution of the chemical compound or element condenses/reacts condenses/reacts and deposits on the surface of the substrate, while the volatile component leaves the reaction chamber. Metal deposition reactions as below in Eqs. (3) and (4).



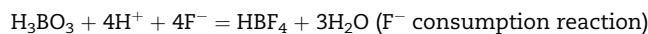
Temperature plays an important role in CVD and usually range between 1100 °C and 350 °C. The chemical reaction that is already in the gas phase leads to precipitate or particle formation. The quality of the thin films mainly depends on the reaction kinetics, preparation of the surface, purity of the precursors, temperature of the reaction, gas flow rate and chamber condition. The deposition can also be carried out in normal or high pressure and also in a vacuum, which makes sure the deposition under inert and low-temperature condition. Plasma activation significantly reduces the reaction temperature required for a reaction to be carried out [48]. In general, the surface deposition is reaction controlled, that is the film growth depends on the angle distribution of the incoming reactants should be very low and to compare with PVD techniques more direction dependent deposition possible [49]. Though CVD techniques have not replaced sputtering or other methods, the difference in microstructures and film defects and density are some of the possible reason that prevails in CVD. In metal deposition technique plasma and low-pressure CVD activated or enhance are most liked methods.

Liquid phase deposition (LPD)

The LPD technique is one of the wet processes for the formation of metal oxide thin films. The advantage of these techniques is that it can form a uniform metal oxide or hydroxide thin film synthesis is possible on various substrates and just by immersing in the aqueous solution of the salts [50]. Thin film of metal oxides formation is possible by means of ligand exchange with a reaction such as hydrolysis, by reaching reaction equilibrium of metal-fluoro complex ($\text{MF}_x^{(x-2n)}$) and the fluoride ion consumption reaction by using boric acid as its scavenger. Further $\text{MF}_x^{(x-2n)}$ the reaction was hydrolyzed with water following ligand exchange equilibrium reaction:



Later the reaction is shifted towards the right-hand side by the addition of boric acid which is F^- ion scavenger, that readily reacts with F^- and forms a stable complex as below,



Thus LPD method is a unique process to prepare various kinds of metal oxide thin films. The LPD is a very simple process and does not require any special kind of instruments that includes a high vacuum system in comparison with gas phase processes. It can be, moreover readily used to various kinds of substrates with large surface areas and complex surface morphologies at ambient conditions [51].

Physico-chemical properties of photocatalytic thin films

Thin films or coating require a non-regular approach to characterization. Variety of techniques has been used for characterizing or analysis the thin film for their composition, surface morphology and in most of the cases, the thickness of the film plays a pivotal role, such that it can alter/influence the

carrier and optical properties. Photons and electrons are some of the probing beans which are favorite methods. Table 2 gives the techniques ordered by incident probe/beam.

Incident photon beam techniques

Surface analysis

The X-ray photons generated can penetrate to several μm deep into the sample (see Fig. 7). But few of the techniques such as XPS is surface sensitive technique owing to its shorter path length of the photoelectron. Photoelectron of kinetic energies of 300 eV–1500 eV is generally used in XPS systems. Due to the short path length, the sample depth is usually between 0.5 nm and 3 nm (almost 3 to 5 atom layer) [52]. The electron intensity can decay atom below the surface and practically ~68 to 10 nm making the nondestructive mode as a function of depth investigation [53]. Usually, the data collected using one of the two modes used. Wide scan (broad scan) or the survey spectra usually gives the data of the entire range. Narrow scans collect the higher energy resolution of the surface and smaller windows are very useful in resolving the chemical state of the compound. Even though the technique is a must for the elemental analysis and mapping, it has some drawbacks that need to be addressed. It requires high vacuum, small analytical area, limited specific organic information and sputtering can be challenging. Fig. 8 gives an overall XPS spectrum of Co_3O_4 nanoparticle that includes wide scan and narrow scan [54].

Crystal structure

X-ray diffraction techniques are one of the versatile and basic techniques to distinguish or to find the crystal structure and phase [55]. Wide angle diffraction technique is widely used in this method and it is related to Bragg's reflections due to the lattice crystals corresponding to 2θ in the range between 5° to 170° for a defined X-ray tube. This description does not require large angles between incident rays or scattered rays to the thin film. But it wide-angle diffraction gives sensitive information about crystal structure, the lattice constant, texture and also strains. This information is obtained by utilizing basic information diffraction angle θ of interference maxima and spacing d of corresponding lattice planes [56].

$2\theta \sin \theta = m\lambda$, Where, m is an integer designating the order of reflection, and λ is the wavelength.

Apart from their strength to distinguish the different phase and strain size, they have some of the drawbacks such as it

can provide only large information and it does require a minimum of 1–5 wt% of the material for phase identification. The thickness of the film cannot be measured and its peak cannot be obtained if there is no electron density difference between lattice planes [6]. Table 3 shows various types of metal oxides and its hybrids based thin film photocatalysts for different photocatalytic applications such as hydrogen production, CO_2 reduction, degradation of organic dyes and bacteria.

Photoluminescent properties

PL and FTIR are the optical spectroscopy techniques used for optical characterization of the materials. The photo luminescence properties of the material are studied through PL spectroscopy studies. The physical principle is described in Jablonski diagram [57]. It also gives an insight into the possible defects in the crystal. It is a process where photons were absorbed by the substance, re-emit the same amount of photons usually as somewhat lower energies. It analyzes the distribution energies involved in the absorption and emission process and because of its nondestructive nature; it can be applied to solids solution, liquids and also gaseous molecules. PL intensity with respect to function time is a wonderful tool to study the lifetime of the electron in the fluorescent material [17]. This technique can offer a time resolution in the order of the laser pulse slit width, as short as femtoseconds [17]. Hence lifetime decay of the fluorescence material can be studied. Thus making PL spectroscopy a versatile technique to study the fluorescent material.

The Fourier transform IR (IR) is another tool which can provide valuable information about the functional groups present or the nature of the materials [58]. IR spectroscopy is the division of optical spectroscopy as it uses region of IR or portion of this spectrum. The spectrum ranges from less than $2 \mu\text{m}$ – $30 \mu\text{m}$ the intensity of the IR spectrum is usually low and it uses the FT spectroscopy to transform the data in a better way in the shorter time [59]. FTIR can be done in both in the air in ambient conditions depending on the type of analysis carried out and it is also possible to monitor the adsorption, absorption (both at the same time) and decomposition process that may occur. Spectra can be either in transmission or absorption modes. Reflectance can also be recorded. Signals that arises from the thin films can be differentiated and compared and also it can be quantified. It can also be used for identifying the film thickness and composition.

Table 2 – Different probing used for different technique and information obtained from them.

Probing Beam	Techniques	Information obtained
Electron	Photoluminescence spectroscopy (PL)	Luminescence properties, defects
	X-ray photoelectron spectroscopy (XPS)	Surface states of chemical and composition of the surface
	X-ray Diffraction (XRD)	Crystal structure and its crystal phase
	Fourier transform infrared spectroscopy (FTIR)	Functional groups on the surface
Other methods	Scanning Electron Microscopy (SEM)	morphology of surface and thickness
	Transmission electron microscopy (TEM)	Micro and nanostructure, atomic structure arrangements
	Energy dispersive electron microscopy (EDS)	Surface composition and its distribution
Other methods	Auger electron microscopy	Surface elemental composition
	Scanning probe methods	Surface roughness and thickness, topography
	Atom probe methods	Atom distribution

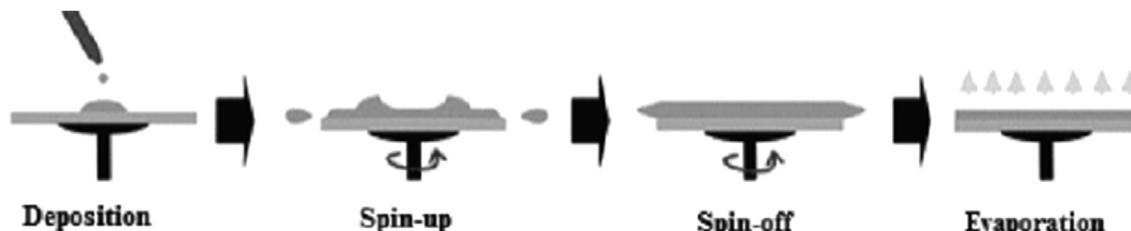


Fig. 7 – Spin coating process. Reprinted with permission from Ref. [41].

Incident electron beam techniques

Morphological characteristics

Scanning electron microscopy techniques are very useful to study the surface topography and structure. The images were produced by accelerating electrons which on bombardment produces secondary or back scattered electrons which are created by scanning the sample surface with a focused electron beam. The energy of the beam usually is between 100 eV and 30 K eV. The image resulting from the secondary electrons can be obtained and collected at a high magnification [60]. Thus can offer a great deal on surface morphology of the material or thin films. The incident electron beam also exerts characteristic X-rays, can be collected and used to collect possible elemental composition information of sample [15]. This can be achieved by using detectors involving energy or wavelength dispersive X-ray. When an incident electron beam strikes sample surface, some of the electrons are back-scattered with the similar or lesser energy and some of the lower secondary electrons are excited, and some Auger electrons are generated and characteristic X-rays excited. Using a different type of detectors for each of these types of electrons generated or photons can be used to construct or determine

the information about the elemental composition of sample [60]. The EDXS, the system collects the X-rays, segregates and also plots them with variation in energy and involuntarily identifies and mark/labels the elements present. The drawback of using the EDXS in thin films analysis is the interaction volume of the sample, the amount substances present on the surface of the substrate and interaction of the substrates may provide the bias results [61].

Size and nanoscale structures

Another versatile electron microscopy technique is transmission electron microscopy (TEM). Electron microscopes are multi-technique instruments that can offer a wide diversity of information about materials including thin films. In principle, the construction of the TEM is a similar light microscope only difference it makes is the use of the electron as the source and resolution. The ordinary optical microscope uses the light as the source which has the wave aberration of 0.3 μ m whereas the TEM has the 0.0025 nm wavelength that is almost equal to the operating energy of 200 kV. Unlike SEM, TEM can provide more useful data, that includes, lattice fringes, lattice spacing, electron diffraction pattern and also crystallinity of sample [62].

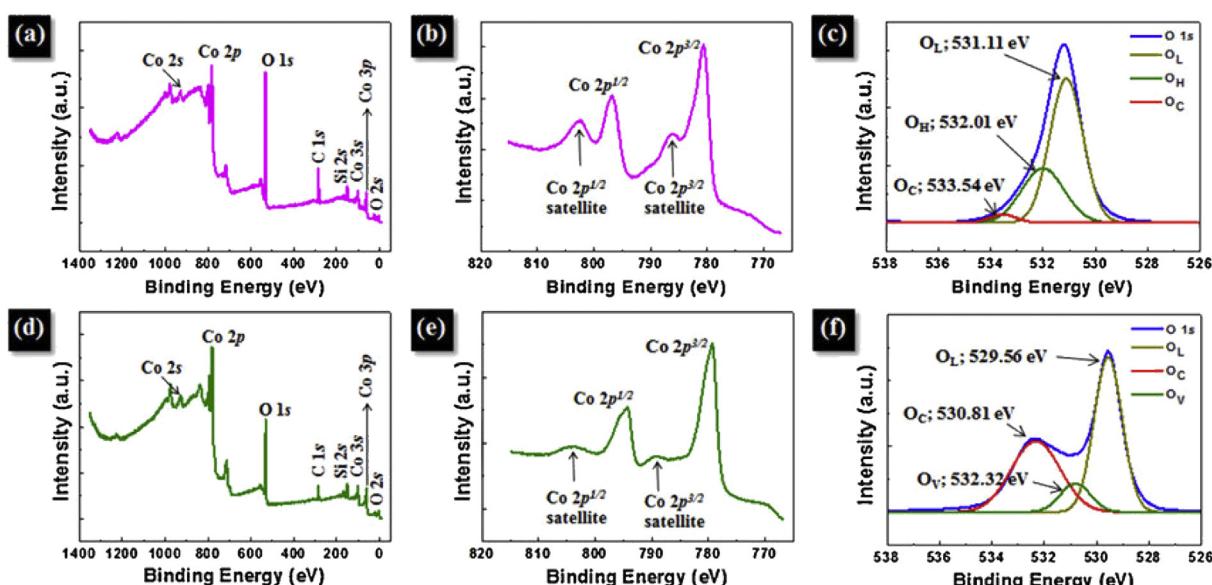


Fig. 8 – (a) Full scan XPS spectra, (b) Co 2p narrow scan spectra, and (c) O 1s narrow scan spectra and its deconvoluted sub-peaks of Co(OH)₂ NPs. (d) Full scan XPS spectra, (e) Co 2p narrow scan spectra, and (f) O 1s narrow scan spectra and its deconvoluted sub-peaks of p-Co₃O₄ NPs. Reprinted with permission from Ref. [54].

Table 3 – Different photocatalytic thin films with application.

Thin films	Applications
TiO ₂ , Ag/TiO ₂ , Fe ₂ O ₃ , WO ₃ , ZnO	H ₂ generation
Carbon modified n-type TiO ₂ /Ag	
Granular alpha-Fe ₂ O ₃	
Cr- and Fe-ion-doped TiO ₂ thin films	
PbS/ZnO hybrid thin film, CuO-TiO ₂ nanotube	
Nanorods/mesoporous/bulk structure TiO ₂	
EBID induced deposition of TiO ₂	Electrochemical H ₂ generation
CdS/ZnS/Ru	Simultaneous H ₂ generation and formic acid degradation
n-type and p-type Cu ₂ O thin films	CO ₂ into CH ₄ and C ₂ H ₄
1D Cu ²⁺ -deposited TiO ₂ nanorod thin films	CO ₂ to methanol and ethanol
Cu _x O- SrTiO ₃	CO ₂ to CO
Electrodeposited catalyst Sn/SnO _x	CO ₂ reduction to HCOOH and CO
TiO ₂ -MnO _x -Pt	CH ₄ and CH ₃ OH
TiO ₂ -anatase films	Photo-catalytic degradation of trichloroethylene
Au-buffered TiO ₂ thin films	Methylene blue degradation
TiO ₂ /SiO _x	Dye degradation
ZnO thin films	Methylene blue degradation
ZnO deposited on silicon	Dye degradation
ZnO nanorods (NRs) grown on a 3 nm ZnO film	Dye degradation
α-Fe ₂ O ₃ thin films on Si (100) substrates	Dye degradation
SrTiO ₃ alpha-Fe ₂ O ₃ thin films	Dye degradation
Fe ₂ O ₃ thin films deposited on SnO ₂	Disintegration of 2-naphthol
PbO/TiO ₂	Stearic acid degradation
Ag/TiO ₂ , C70-TiO ₂	Bacterial disinfection
Al ₂ O ₃ -doped TiO ₂ , N-doped TiO ₂	Escherichia coli (E.coli) and Staphylococcus aureus (S.aureus) disinfection
S-doped and N,S-co-doped	E.coli, S.aureus and Streptococcus pyogenes
TiO ₂ -Ag films	P.aeruginosa disinfection
Ti _{1-x} Nb _x N-Ag films	E.coli disinfection

The main point of the TEM is for the image interpretation for it is required to understand image contrast formation. Specimen information is responsible for the strong scattering which appears dark in the electron microscopic image. The aperture size determines the scattering-absorption contrast, and therefore it is called as "contrast aperture". If this aperture is moved in such a way that instead of the unscattered beams the more of the deflected rays go through. Then all of the sample areas which scatter weakly appear dark, whereas those responsible for a strong deflection are bright ("dark field imaging") [63]. A substrate is also an important tool; in here the thin films can be easily deposited on it and can be easily analysis both cross-section as well as the plain view. High-resolution TEM is another version of the TEM, where the images can be obtained at an atomic level. Inter-atomic distance and also lattice mismatch can be easily analyzed using HRTEM. The lattice mismatch of the two different materials can be analyzed and distance and size can be measured. Usually, the TEM can be equipped with EDAX for the imaging the single particle for their elements and other contents.

Other characteristics

Surface properties at the atomic level

SPM technique is a section of microscopy that had been developed in multiple functional ways to provide a nanometer resolution regarding the properties of the thin films and also other materials. It includes the topography, roughness, hardness and also conductivity of the material. Images are formed due to the interaction of the probe with the surface,

mechanically scanned from corner to corner of the surface. It scans in a raster pattern whereas it keeps the track of the probe and sample interaction as a function of the position of the tip. Depending on the probes that are used, different scanning techniques can be utilized. The two methods that are most common are STM and AFM, and AFM is often called as scanning force microscopy (SFM). There are 20 different methods/techniques have been developed using these techniques. The probe is the very important part of the instrument, and there is a different probe for a different type of the sample based on the resolution and thickness the probe can be changed for better resolution. The resolution of these techniques differs depending on the required type of interface utilized and in some of the cases, atomic range resolution is attainable. Scanning tunneling microscopy (STM) is a powerful method that facilitates the imaging of the conductive sample surface down to the range of atomic level. The STM technique is based on the quantum tunneling of the electrons between two surfaces as they are brought to close proximity sufficiently then their electrons clouds begin to overlap on one another.

The electrode tip is atomically sharp is placed within few nm distances from the surface and low tip voltage bias probes the density of the electronic states of the atoms comprising the sample surface by monitoring the tunneling current generated due to the positioning of the sample and probe [64].

On the other side AFM unlike STM, where the tunneling current between the electrode and the sample was recorded, in AFM images are produced. Laveena et al., demonstrated the interaction between a dye and quantum dots and their hybrid

structure using AFM [64]. Fig. 9 shows the AFM images of the interaction between dye, CdSe QDs, and TiO₂. AFM supervises the force between the tip and surface of the sample and uses this force generated to produce images. AFM is a very important tool for analyses the surface topography of thin films.

Photocatalytic applications of nanostructured semiconductor thin films

Hydrogen generation

Hydrogen is an ultimate clean and renewable energy vector and is pollution free. There are various semiconductor photocatalytic and electrocatalytic thin films were used for evolution of H₂ such as mesoporous TiO₂, Ag/TiO₂, Fe₂O₃, WO₃, ZnO etc. The mesoporous titania thin films deposited on fluorine-doped tin oxide (FTO) electrodes were tested for water splitting under visible light [66,67]. Carbon modified

n-type TiO₂ (CM-n-TiO₂), Ag/TiO₂ nanocomposite on pyrex wafers was employed for H₂ generation under UV light, which generates 147.9 ± 35.5 mmol/h/g of H₂, however without Ag, it was found to decrease dramatically to 4.65 ± 0.39 mmol/h/g for anatase TiO₂ films and to 0.46 ± 0.66 mmol/h/g for amorphous TiO₂ films attributed to visible light activity of Ag/TiO₂⁴⁶. Wei et al. [68] analyzed the effect of the different morphologies on water splitting capability. Hydrogen evolution rate for granular alpha-Fe₂O₃ films was higher compared to alpha-Fe₂O₃ powder and TiO₂ catalysts, which is attributed to the porous nature of the films, which increases the specific surface area. Tan et al., reported the sputtering technique to deposit the Ru nanoparticle on graphene sheet for enhanced hydrogen production. Ru/Graphene material showed enhanced electrocatalytic catalytic activity for H₂ production and dehydrogenation of NaBH₄. The physical sputtering technique is very efficient in formation of Ru nanoparticle on the surface of graphene [69].

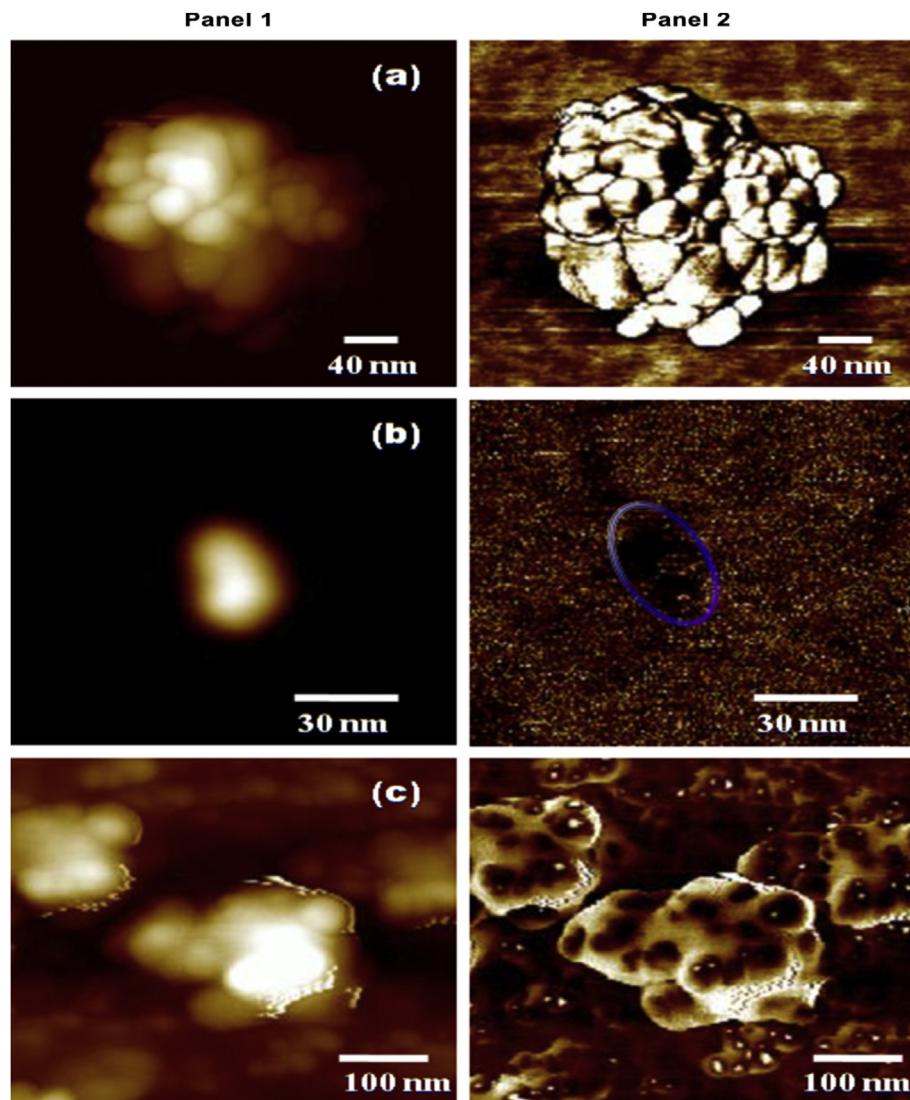


Fig. 9 – AFM images of (a) TiO₂, (b) TiO₂/N719 dye and (c) TiO₂/N719 dye–CdSe QD, Panel 1 is the height image and Panel 2 is the phase image of the above. Reprinted with permission from Refs. [64,65].

Huang et al. prepared photocatalytic TiO_2 thin films via an electron beam-induced deposition (EBID) method, which showed an hydrogen and oxygen evolution of 59.8 and 30.6 μmole , respectively, after 8 h of reaction under UV irradiation [70] with a photocurrent of 2.1 mA was observed for the TiO_2 thin film with post-calcination at 500 °C whereas 700 °C calcined thin films showed bad adhesion which results in poor photocatalytic performance. Cr- or Fe-ion-doped TiO_2 thin films by radio-frequency magnetron sputtering and a sol–gel method showed higher H_2 production rate ($\mu\text{mol/h}$) for Fe-doped TiO_2 (15.5 $\mu\text{mol/h}$) than for Cr-doped TiO_2 (5.3 $\mu\text{mol/h}$) due to the ability of Fe ions to trap both electrons and holes, thus avoiding recombination, while Cr can only trap one type of charge carrier [71]. Dholam et al. reported TiO_2 thin films prepared by radio-frequency magnetron sputtering and sol–gel method for hydrogen generation by photocatalytic water splitting under visible light irradiation and concluded sputter-deposited film as compared to sol–gel synthesized film showed better H_2 generation rate, mainly because of the higher visible light absorption achieved by oxygen vacancies created in the TiO_2 film by the energetic target ions during deposition in pure Ar gas pressure [72]. Xu et al., demonstrated the generation of hydrogen using moisture from the air. They developed a solid state electrochemical cell, replacing the liquid electrolyte with proton conducting polymers. The anode was supplied with 80% relative humid air and argon at the cathode, where Pt/C cathode was replaced with 2D C_3N_4 and placed tandem to photoanode. Tandem configuration showed the 3 fold increase in hydrogen production [73].

PbS/ZnO thin film was designed by Jaim et al. for the photocatalytic hydrogen production where p-type PbS thin film was prepared by chemical bath deposition onto a glass substrate, followed by an n-type ZnO thin film deposition by RF magnetron sputtering. The results showed a higher photocatalytic hydrogen production of PbS/ZnO thin film ($7.38 \mu\text{mol cm}^{-2}\text{h}^{-1}$) compared to PbS ($3.35 \mu\text{mol cm}^{-2}\text{h}^{-1}$) and ZnO ($2.45 \mu\text{mol cm}^{-2} \text{h}^{-1}$) thin films and linear sweep voltammetry (LSV) test showed the synergistic effect between PbS and ZnO thin films for the generation and transport of the charge carriers [74]. Huang et al. compared nanorods (NR- TiO_2), mesoporous (MP- TiO_2), and bulk structure (BK- TiO_2), prepared by evaporation induced self-assembling process or electron beam induced deposition method. Under UV-light irradiation, a highest net photocurrent of 0.747 mA was observed for the NR- TiO_2 thin film with hydrogen and oxygen yields of 35.8 and 17.2 μmole , respectively after 8 h for NR- TiO_2 due to larger surface area and the lower concentration gradient of the solution. BK- TiO_2 and MP- TiO_2 demonstrate that TiO_2 thin film with the higher crystallinity showed better performance in both photocurrent and water splitting reaction [75]. CdS/ZnS/Ru catalyst film by chemical bath deposition showed higher hydrogen production of $123 \mu\text{mol/m}^2/\text{h}$ under visible light and $135 \text{ mmol/m}^2/\text{h}$ under the simulated solar light together with simultaneous degradation of formic acid. ZnS layer suppresses recombination together with improving the stability of CdS and Ru further improved the photocatalytic activity [76]. Nalajala et al. compared powder and thin film form of TiO_2 photocatalyst for H_2 evolution and suggests that

1 mg thin film form of Pd/ TiO_2 (P25) yields 11 to 12 times higher H_2 production compared to its 25 mg powder form (Fig. 10(B)). The increased light absorption by most of the catalyst coated in the form of thin film results in enhanced surface area utilization for photocatalysis. In the particle form, equal light absorption by all the photocatalyst with more volume of reactant is not possible (see Fig. 11).

Photocatalytic CO_2 reduction to valuable chemicals

Quick expansion of industry increases the requirement for energy. The burning of fossil fuel leads to enhancement in the CO_2 concentration in the environment. An improved amount of CO_2 is the main origins of global warming, which results in enormous natural disasters. Therefore capturing and utilizing CO_2 for renewable energy and environmentally application are an important research topic. n-type and p-type Cu_2O thin films deposited on a Cu substrate converts CO_2 into CH_4 and C_2H_4 with higher selectivity for C_2H_4 due to the mutual contribution from Cu_2O and dotted Cu nanoparticles [77]. Cu^{2+} -deposited TiO_2 nanorod thin films fabricated by a combination of hydrothermal and ultrasonic aided sequential cation adsorption method was studied for the photocatalytic reduction of CO_2 under UV light, which gives methanol and ethanol as main products. 0.02 M Cu^{2+} gives a maximum yield of $36.18 \text{ mmol/g.cat/h}$ of methanol and $79.13 \text{ mmol/g.cat/h}$ of ethanol at a flow rate of 2 mL/min and under the reaction system temperature of 80 °C. The highly efficient photocatalytic activities of $\text{Cu}^{2+}-\text{TiO}_2$ nanorod thin films were attributed to the incorporation of Cu^{2+} ions and one-dimensional (1D) nanostructure which improved the limitations of photon transfer. Cu^{2+} ions served as active sites of electron traps, which could suppress the electron-hole recombination and doping of Cu^{2+} decreases the band gap of TiO_2 . The significantly enhanced CO_2 photoreduction rates were due to the synergistic combination of Cu^{2+} deposition, the high surface area of TiO_2 nanorods and enhanced mass transfer of optofluidic planar reactors (OPMR) [78]. Shoji et al. reported photocatalytic conversion of CO_2 into CO utilizing H_2O as an electron donor using $\text{Cu}_{x}\text{O}-\text{SrTiO}_3$ under UV irradiation. The improved reduction can be attributed to Cu_{x}O clusters loading and the high conduction band of SrTiO_3^{79} .

Chen et al. reported that the electrodeposited catalyst Sn/SnO_x exhibited greatly enhanced CO_2 reduction catalysis relative to a typical Sn foil electrode with a native SnO_x layer. For both electrodes, CO, HCO_2H , and H_2 together accounted for >99% of the reduction products in $\text{NaHCO}_3/\text{CO}_2$ electrolyte [80].

$\text{TiO}_2-\text{MnOx-Pt}$ composite with the surface junction between [81] the [82] facets, MnO_x nanosheets, and Pt nanoparticles are selectively deposited on each facet by a facile photo-deposition method. This design forms two heterojunctions: metal-semiconductor junction between Pt and TiO_2 and the p-n junction between MnO_x and TiO_2 [82] facet. Both of them, along with the surface heterojunction between the facets, leads to reduced recombination. Because of their combined effect, the composite photocatalyst shows an improved yield of CH_4 and CH_3OH , which is three times of pristine TiO_2 nanosheets films [83] (see Fig. 12)

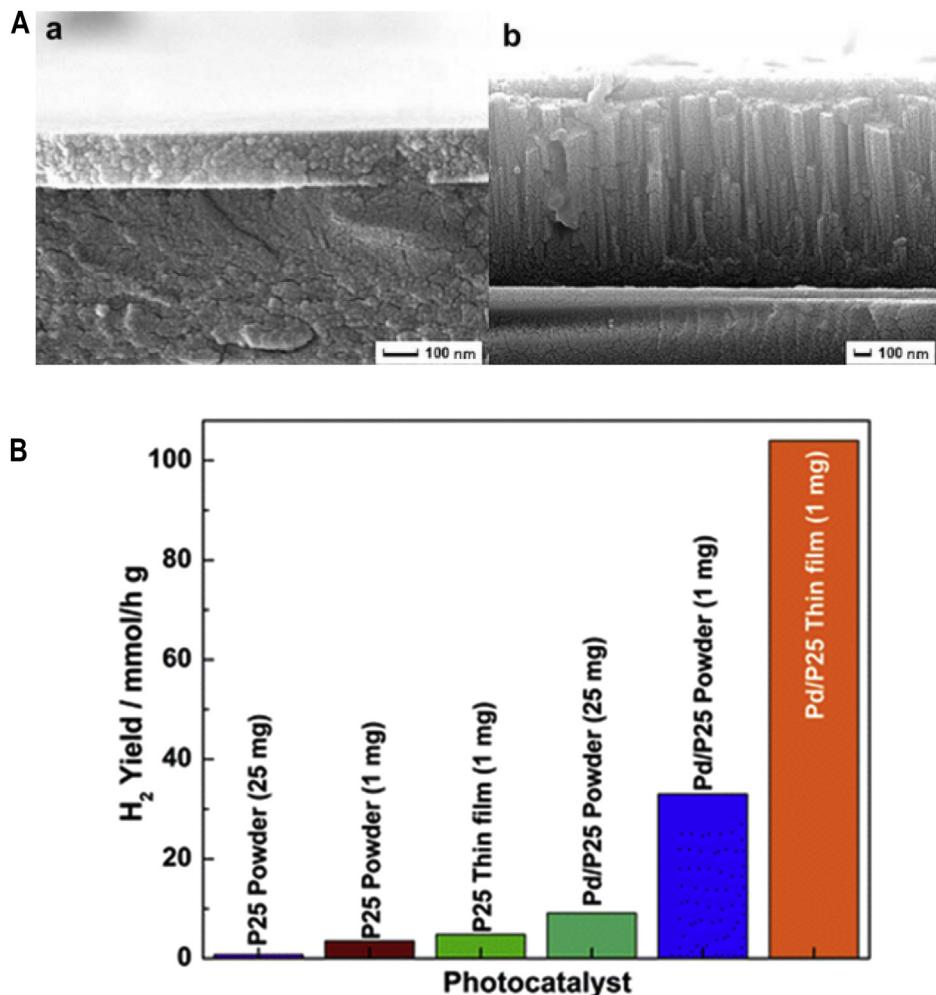


Fig. 10 – A. SEM micrographs of a cross-section of TiO₂ deposited by a) sol-gel b) RF magnetron sputtering. Reprinted with permission from Refs. [66a,72]. B. Photocatalytic hydrogen generation with powder and thin film TiO₂ P25 catalyst.

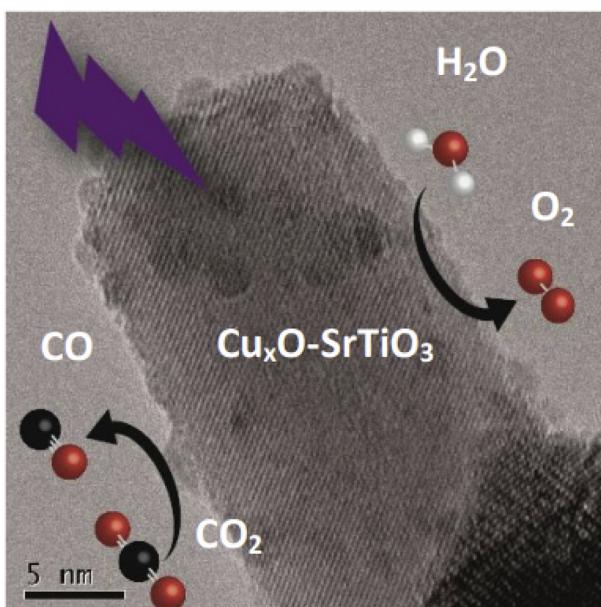


Fig. 11 – Mechanism of CO₂ reduction on Cu_xO-SrTiO₃. Reprinted with permission from Ref. [79b].

Water treatment/degradation of toxic organic dyes

Sol-gel synthesized porous TiO₂-anatase films showed improved photo-catalytic degradation of trichloroethylene (TCE) in comparison to titania films. Titania sols prepared along with a pore-generating agent, polyethylene glycol demonstrated the highest specific surface area ($S_s = 43 \text{ m}^2/\text{g}$). Porous TiO₂- demonstrates around 20% more TCE conversion compared to dense films. Porous volume, surface area, and thickness of the coating play a key role in the photocatalytic activity. High porosity and surface area incriminate higher contact with a surface exposed to TCE thus improves the rate of degradation [84]. Baradarhan et al., demonstrated the effect of Al concentration on ZnO thin film towards photocatalytic activity. The incorporation of Al in between ZnO increases the bandgap and thus increasing the photocatalytic activity of degradation of methylene blue by 95.2% [85]. Fig. 13 shows the fabrication process and enhancement of photocatalytic activity of TiO₂ with combination of MnO₂ an Pt particles.

Au-buffered TiO₂ thin films synthesized through radio frequency magnetron sputtering process showed 50% enhancement in the photocatalytic activity for methylene

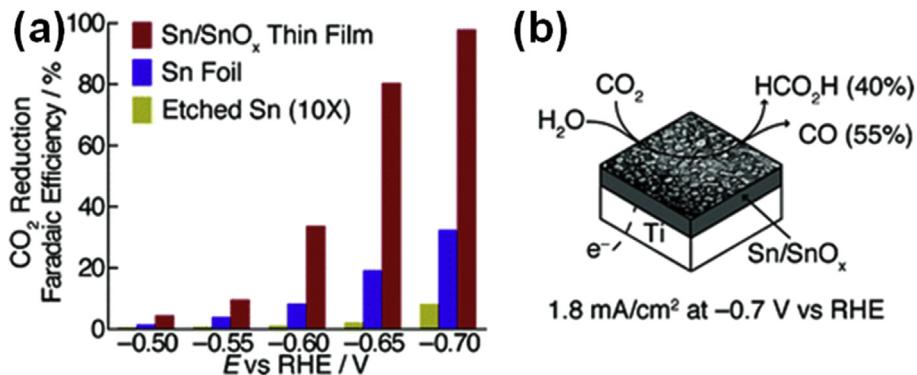


Fig. 12 – a) CO₂ reduction efficiency by Sn/SnO_x b) Mechanism of CO₂ reduction. Reprinted with permission from Ref. [77].

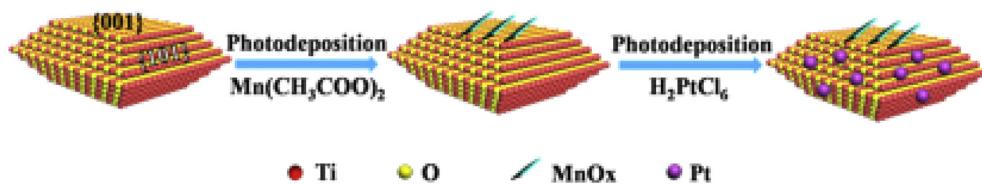


Fig. 13 – The selective photodeposition process of MnO_x nanoflakes and Pt on anatase TiO₂ (001) and (101) facets. Reprinted with permission from Ref. [83].

blue degradation. Calcination of Au-buffered TiO₂ at 600 °C reduces the film roughness, but its enhanced specific surface area and anatase crystalline size, increases the photocatalytic activity. Sakthivel et al. [86] claims that photocatalytic effectiveness is related to the amount of Au, Pt, Pd. Additionally, uniform distribution of Ag microgrid and Au nano-aggregates on TiO₂ surface enhances the photoactivity. Amorphous Au-buffered TiO₂ thin films show higher photocatalytic activity compared to pure anatase TiO₂ thin films attributed to reduced recombination of charge carriers by Au buffer layer. Hence more holes remain for production of hydroxyl radicals, thus improving the photodegradation [87].

The polymer Tedlar, composed of polyvinyl-fluoride units ($-\text{CH}_2-\text{CHF}-$)_n and parylene, a fluoro-polymer generally depicted as ($-\text{CH}_2\text{CHFCH}_2\text{CHF}-$)_n supported TiO₂ showed about two times higher activity for photocatalytic degradation of azo-dyes compared to polyethylene (made up of low-density LDPE)/TiO₂. ⁸³TiO₂/SiO_x double-layers prepared by RF magnetron sputtering induces Ti³⁺ and enhanced photocatalytic action in the double-layer structure is due to presence of Ti³⁺ sites and bandgap combination between TiO₂ and SiO_x. PL results showed improved charge carrier separation of the electron-hole pairs in the double-layer structure, which is dependable with the photocatalytic activity of the samples [88].

ZnO thin films with different thickness deposited by atomic layer deposition were tested for methylene blue degradation to understand the relationship involving the thickness and photocatalytic effect of the films. The photocatalytic activity increases with the thickness, due to the improved charge carries generation by photo-absorption. Conversely, the photocatalytic activity begins to saturate for 20 nm film thickness. In order to transfer the process on a

flexible support, ZnO was deposited on polymethyl methacrylate and silicon.

ZnO deposited on silicon showed higher crystallinity with enhanced MB degradation indicating the importance of the crystallinity for the photocatalytic activity. Furthermore, ZnO nanorods (NRs) grown on a 3 nm ZnO film showed improved photocatalytic activity in comparison to 30 nm ZnO film which is attributed to higher film thickness, which reduces the light absorption [89]. Chen et al. [90] studied the effect of thickness using RF magnetron sputter coated α -Fe₂O₃ thin films on Si (100) substrates and claims enhanced photoactivity with

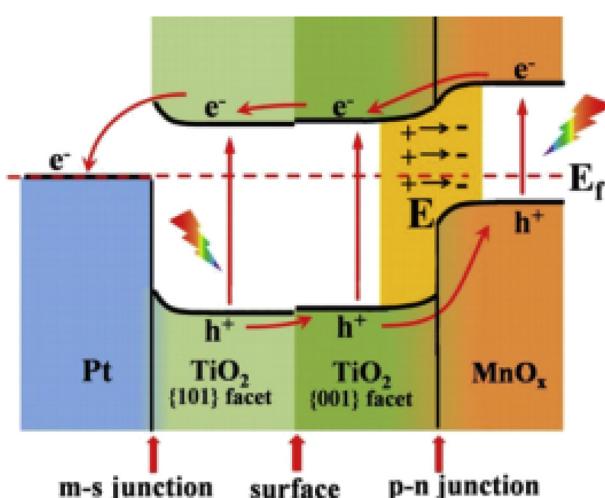


Fig. 14 – Mechanism of charge carrier transfer in TiO₂-MnO_x-Pt composite. Reprinted with permission from Ref. [83].

higher film thickness attributed to improved crystallite size resulting higher surface roughness and lower band gap values. Fig. 14 shows photocatalytic mechanism of TiO₂/MnO₂/Pt hybrid for the photocatalytic reduction of CO₂.

Andrew et al. [91] investigated the effect of the substrate on the photochemical activity of alpha-Fe₂O₃ thin films deposited on SrTiO₃ and alumina substrates. SrTiO₃ showed better photocatalytic activity attributed to the substrate structure, which leads to a lowering of charge recombination and an enhancement in catalytic action. Tetsuro et al. [92] prepared Fe₂O₃ thin films deposited on SnO₂-coated glass substrates through a metal organic deposition process, which showed 20% improved disintegration of 2-naphthol under anodic biased conditions, which is due to reduced recombination achieved by removal of electrons from the Fe₂O₃ surface by the application of an anodic voltage [89,93]. Bhanu et al. prepared PbO/TiO₂ composite films through aerosol-aided chemical vapor deposition, which showed 2 times higher stearic acid degradation compared to previous reports attributed to visible range absorption of PbO/TiO₂ composite film [94]. Fig. 15 shows photodegradation mechanism of Au/TiO₂ hybrid thin film prepared using magnetron sputtering process.

Bacterial disinfection by photocatalytic thin films

Irradiation of photocatalyst generates an electron/hole pair which reacts with surface water to produce hydroxyl radicals which are potent oxidants causes disruption of bacterial membrane followed by the death of bacteria as represented in Fig. 16. Several photocatalyst thin films were evaluated for bacterial disinfection such as TiO₂, Ag/TiO₂, C70-TiO₂ [95] etc and few are listed here (see Fig. 17).

The TiO₂ thin films deposited on glass fiber through a sol-gel dip-coating technique at ambient temperature shows 95% degradation at UV light irradiation, the degradation efficiency was dropped to below 60% in the absence of UV light [94,97,98]. N-doped TiO₂ has a potential antimicrobial surface that can kill Gram-negative Escherichia coli, (E. coli) and Gram-positive Methicillin-resistant Staphylococcus aureus (S. aureus including MRSA) [99]. Hence, which can be implemented in health care. N-Doped TiO₂ is an effectual antimicrobial agent against a number of human pathogens, these include S. aureus, E.coli, and Streptococcus pyogenes. [100]. S-Doped and

N,S-co-doped as well as other enhanced N-doped systems using metals and carbon [101] also have shown antibacterial activity. Oskal et al., reported the inactivation of pathogens like E. coli and Enterococcus faecalis. They claimed the use of plate reactor configuration with immobilized titanium isopropoxide based thin films. They also investigated the antibiotic profile of the target bacteria, with 99% disinfection in 180 min and 99.9% at 240 min of time [102].

Al₂O₃-doped TiO₂ thin film on Corning glass substrate was employed for the photocatalytic elimination of E. coli, which shows alumina doping further increases the inactivation of E.coli. TiO₂, porous TiO₂ (TiO₂-PEG) and TiO₂-Ag films coated on glass fiber synthesized by sol-gel method showed 57%, 93%, and 100% antibacterial effect in 15 min under UV irradiation against P.aeruginosa bacteria, which is attributed to reduced recombination of electron-hole pairs and polyethylene glycol (PEG) increase surface activation site [103]. ⁹⁸C₇₀ modified TiO₂ (C₇₀-TiO₂) hybrid showed proficient photocatalytic disinfection of Escherichia coli O157:H7 in the presence of visible light ($\lambda > 420$ nm) irradiation. Disinfection test illustrates that 73% of E. coli O157:H7 destruction happened in 2 h with a disinfection rate constant of $k = 0.01 \text{ min}^{-1}$, which is three folds better than measured for TiO₂⁹⁹ and the motive for the improved inactivation in C₇₀-TiO₂ hybrid is higher adsorption ability in the visible light region of carbon dots, such as fullerenes (C₆₀ and C₇₀) and carbon nanotubes, which augment the visible light adsorption efficiency of C₇₀-TiO₂ hybrid.

Rtimi et al. reported antibacterial activity of Ti_{1-x}Nb_xN-Ag films acquired by an appropriate combination of low-energy and high-energy sputtering against E.coli, additionally incorporation of Ag further enhances the inactivation process. The inactivation is due to higher visible light absorption and interfaces charge transfer between the photo catalysts [104].

Industrial feasibility and economic aspects of different photocatalytic hydrogen-production technologies

There is essentially three types of processes based on the photo-assisted techniques towards hydrogen production, (i) photocatalysis, (ii) photoelectrochemical and (iii) photobiological process [105]. As it is known that the solar light is the robust source of renewable energy, which can be the most promising way for sustainable hydrogen production through these photo-assisted techniques. As discussed in this review paper, the photocatalytic process involves a suitable light source to activate the photo-active semiconductor to produce H₂ via water splitting [106]. On the other hand, in photo-electrochemical, the electrode will be made in such a way that it can create the electrical potential on its own when it is irradiated under sunlight as shown in Fig. 18(a) and (b)[105].

Technically, the band gap of the photo-active semiconductor should be higher than the limit of 1.23 eV to split water molecules and should overcome the electrical resistance of the closed-circuit [107]. Later, based on this concern, a small amount of external bias is used to boost the electrode potential in order to enhance the photoelectrochemical (PEC) process. In recent times, the design of PEC is improved by creating a device using cathode, anode and photovoltaic

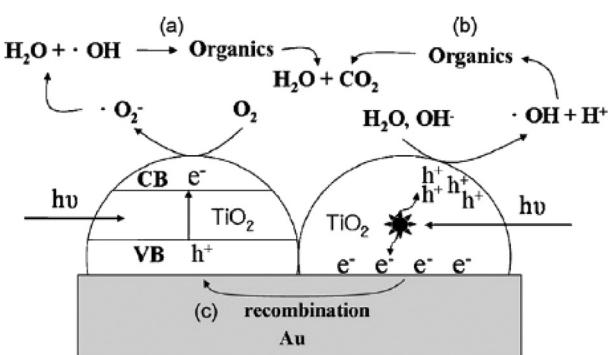


Fig. 15 – Photodegradation by Au-buffered TiO₂ thin films.
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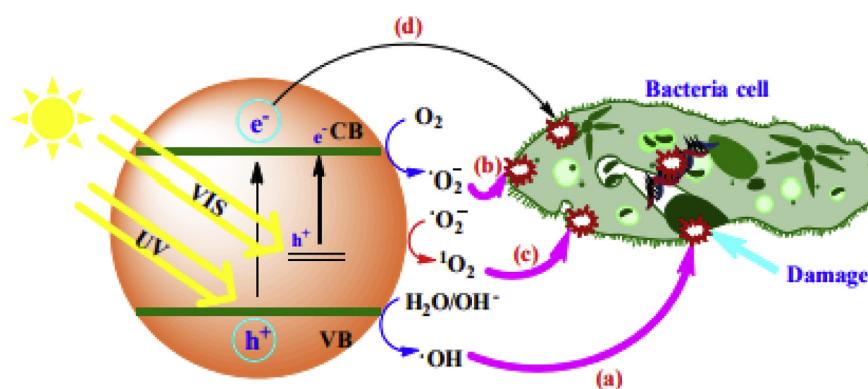


Fig. 16 – Mechanism of bacterial disinfection by semiconductor thin films. Reprinted with permission from Ref. [96].

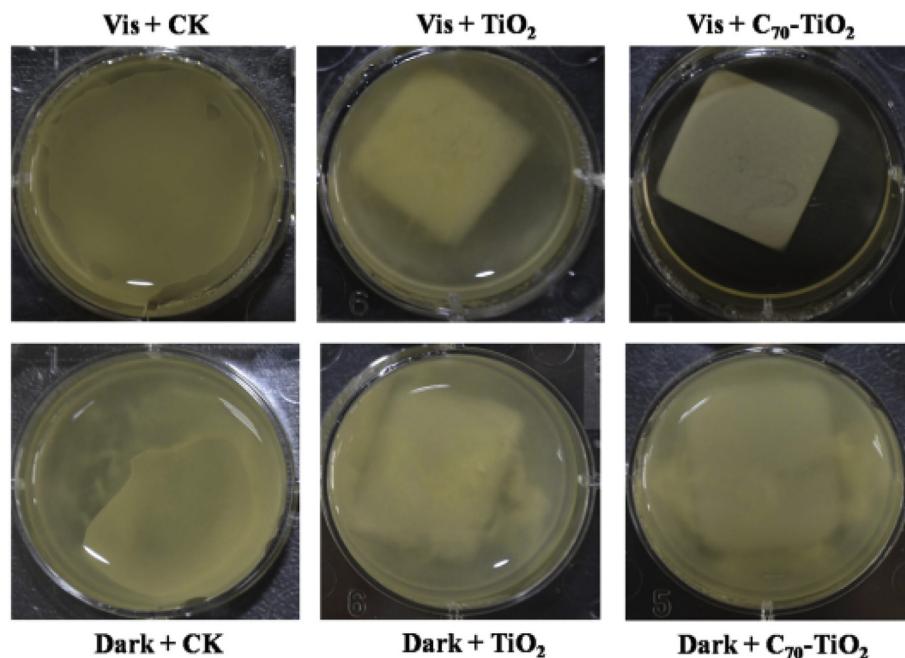


Fig. 17 – *E.coli* O157:H7 biofilm inhibition by TiO_2 and $\text{C}_{70}\text{-TiO}_2$. (CK refers to control). Reprinted with permission from Ref. [101].

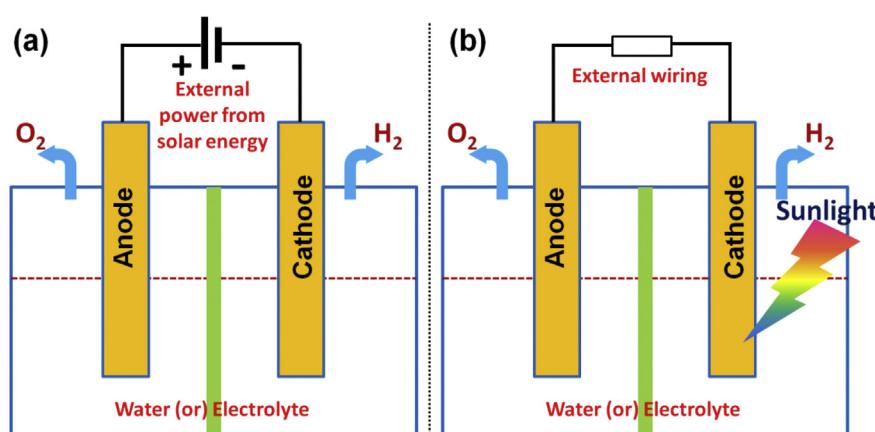


Fig. 18 – (a) Electrolysis, and (b) photo-electrolysis system for H_2 production.

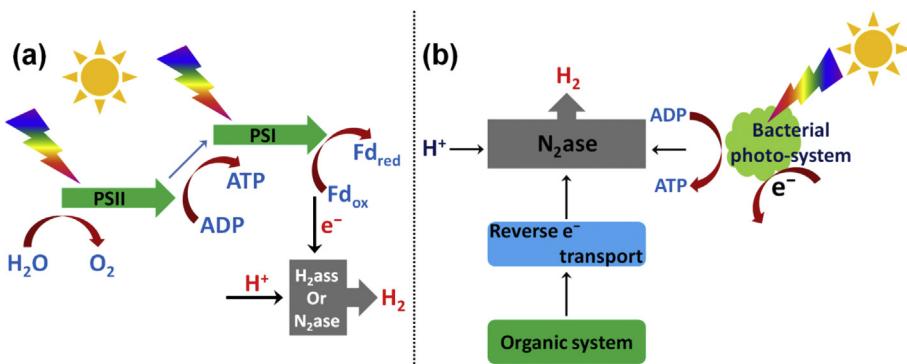


Fig. 19 – (a) Bio-photolysis of green-algae/cyanobacteria, and (b) photo-fermentation by photo-synthetic bacteria for H_2 production.

components layered together as a single system and kept in the water solution to produce H_2 [108]. However, considering the use of solar light and other key challenges in the structure and operating complexity of the system, it can be highlighted that a significant amount of research and development should be necessary towards the commercialization of hydrogen production through PEC process.

In the photobiological process, the water-splitting will be performed using the oxygenic and/or anoxygenic photosynthetic microorganisms in anaerobic conditions. This technique could be effective to produce hydrogen even from waste-water. However, it has an issue of the formation of CO_2 when the anoxygenic bacteria are employed in the reaction [109]. Alternatively, the oxygenic bacteria are largely used to produce H_2 , but the yield is considerably less via this process. The photobiological process can be categorized into (i) direct-biophotolysis, (ii) indirect-biophotolysis and (iii) photo-fermentation. The former process can produce H_2 directly from water via photosynthesis using microalgae. In the latter process (indirect), H_2 can be produced using the system of microalgae and cyanobacteria photosynthesis process. The third process i.e. the photo-fermentation is a process of exploiting a diverse group of photosynthetic bacteria to fermentative-conversion of organic substrates under solar light into H_2 and CO_2 , as shown in Fig. 19(a) and (b) [109,110].

Currently, there are several options commercially available for hydrogen production. In the early stages, the usage of fossil fuels was in the practice to produce hydrogen in large-scale systems. However, it led to the rapid increase of the emissions of greenhouse gases [111]. From a technology-economic perspective, the steam-reforming of natural gas is recognized as the most viable method for hydrogen production. But, the major concern of this process is the cost of natural gas. Considering the photo-assisted techniques, there is no commercialization for the production of hydrogen to date [112]. However, hydrogen production from photo-assisted techniques is possible to be an economically viable option due to the usage of solar light as a major energy resource, which is renewable [113]. The H_2 production through photo-assisted techniques makes it enable to use of the low-grade products. In spite of this promising approach, it still possesses many technological restrictions. Comparing the

different technologies for hydrogen productions, the photo-assisted technique is environmentally benign option and constructive alternative for the enhanced and large-scale production of hydrogen [114]. Eventually, this photo-assisted technology would possibly play the major and significant role in the near future, which crucially needs for the greener environment and hydrogen energy-based economy.

Future prospective

The future developments in the field of photocatalytic thin films largely lie in enhancing their interfacial functional properties and subsequent features. Thin films of photocatalytic materials fabricated either on a substrate or as free-standing structures promisingly carry potential in terms of its multifunctional interfacial interactions and tunable properties. Thin film structuring of conventional photocatalysts creates a huge basis that endows with versatile catalytic, chemical, and electronic properties. The features offered by thin films owing to their excellent flexibility, stability, and multifunctional properties are already inspiring and has been a subject of numerous and diverse fields of science and technology in health care, energy, and environment. There are essentially three stages where the extensive research is required, (i) material developments, (ii) fabrication and (iii) industrial implementation of photocatalytic thin films. Apart from the conventional metal oxide based materials, the other potential photocatalytic materials such as inorganic perovskites, metal-organic frameworks, etc., have to be fabricated as thin film materials for the photocatalytic process. Similarly, fabrication of free-standing thin films is highly required for their successful implementation in industrial scale applications. In this direction, photocatalytic materials require simplicity in devising them in large scale. Thin film structures are most appropriate for such a process. Especially, reactor designs for the photocatalytic process are greatly important for industrial applications.

The conventional powdered photocatalytic materials require separate attention to handle them in all levels of the photocatalytic process, which includes synthesis, dispersion

in the medium, recyclability, recovery, and disposal. Moreover, the reactors also need to be optimized for their other parameters such as light irradiation, temperature, the basis of a photocatalyst in the reactor, etc. Considering these aspects, the perspective of thin films should be largely focused on their implementation for industrial applications along with the reactor designs. Thin films have created revolutionary impact in the field of solar cells and therefore the meticulous understanding of thin film structures and their properties towards photocatalytic applications can also create significant impact in the field of photocatalytic science and technology towards large-scale energy and environmental applications.

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REFERENCES

- [1] Mortazavi B, Madjet ME, Shahrokh M, Ahzi S, Zhuang X, Rabczuk T. Nanoporous graphene: a 2D semiconductor with anisotropic mechanical, optical and thermal conduction properties. *Carbon* 2019;147:377–84.
- [2] Liu Y, Li C, Li B, Song H, Cheng Z, Chen M, He P, Zhou H. Germanium thin film protected lithium aluminum germanium phosphate for solid-state Li batteries. *Advanced Energy Materials* 2018;8(16):1702374.
- [3] Yu J, Sun D, Wang T, Li F. Fabrication of Ag@AgCl/ZnO submicron wire film catalyst on glass substrate with excellent visible light photocatalytic activity and reusability. *Chem Eng J* 2018;334:225–36.
- [4] Reddy KR, Hassan M, Gomes VG. Hybrid nanostructures based on titanium dioxide for enhanced photocatalysis. *Appl Catal Gen* 2015;489:1–16.
- [5] Yana D, Fua X, Shang Z, Liua J, Luo H. A BiVO₄ film photoanode with re-annealing treatment and 2D thin Ti₃C₂T_X flakes decoration for enhanced photoelectrochemical water oxidation. *Chem Eng J* 2019;361:853–61.
- [6] Ravikumar CH, Nair GV, Muralikrishna S, Nagaraju DH, Balakrishna RG. Nanoflower like structures of MoSe₂ and MoS₂ as efficient catalysts for hydrogen evolution. *Mater Lett* 2018;220:133–5.
- [7] Roy A, Movva HC, Satpati B, Kim K, Dey R, Rai A, Pramanik T, Guchhait S, Tutuc E, Banerjee SK. Structural and electrical properties of MoTe₂ and MoSe₂ grown by molecular beam epitaxy. *ACS Appl Mater Interfaces* 2016;8(11):7396–402.
- [8] (a). Wei B, Liang H, Qi Z, Zhang D, Shen H, Hua W, Wang Z. Construction of 3D Si@Ti@TiN thin film arrays for aqueous symmetric supercapacitors. *Chem Commun* 2019;55:1402–5.
(b). Ganpule CS, Stanishevsky A, Aggarwal S, Melngailis J, Williams E, Ramesh R, Joshi V, Araujo CPD. Scaling of ferroelectric and piezoelectric properties in Pt/SrBi₂Ta₂O₉/Pt thin films. *Appl Phys Lett* 1999;75(24):3874–6.
- [9] Dolors P, Carmen J, Mónica B. Engineering of functional manganites grown by MOCVD for miniaturized devices. *Adv Mater Interfaces* 2017;4(8):1600974.
- [10] Chen X, Zhang G, Wan J, Guo T, Li L, Yang Y, Wu H, Liu C. Transparent and flexible thin-film transistors with high performance prepared at ultralow temperatures by atomic layer deposition. *Adv Elect Mater* 2019;5:1800583.
- [11] Lia G, Shen Q, Yang Z, Kou S, Zhang F, Zhang F, Guo H, Du Y. Photocatalytic behaviors of epitaxial BiVO₄(010) thin films. *App Catal B: Environ* 2019;248:115–9.
- [12] Basavarajappa PS, Seethy BNH, Ganganagappa N, Eshwaraswamy KB, Kakarla RR. Enhanced photocatalytic activity and biosensing of gadolinium substituted BiFeO₃ nanoparticles. *Chem Select* 2018;3:9025–33.
- [13] Francis O, Kuben GK, Elizabeth van Sittert CGC, Poomani GP. Recent progress in the development of semiconductor-based photocatalyst materials for applications in photocatalytic water splitting and degradation of pollutants. *Adv Sustainable Systems* 2017;1(7):1700006.
- [14] Reddy KR, Reddy CV, Nadagouda MN, Shetti NP, Jaesool S, Aminabhavi TM. Polymeric graphitic carbon nitride (g-C3N4)-based semiconducting nanostructured materials: Synthesis methods, properties and photocatalytic applications. *J Environ Manag* 2019;238:25–40.
- [15] Ravikumar CH, M, S, Mahto A, Nanjundaiah RT, Thippeswamy R, Teixeira SR, Balakrishna RG. Observation of oxo-bridged yttrium in TiO₂ nanostructures and their enhanced photocatalytic hydrogen generation under UV/Visible light irradiations. *Mater Res Bull* 2018;104:212–9.
- [16] D'Souza LP, Muralikrishna S, Chandan HR, Ramakrishnappa T, Balakrishna RG. Neodymium doped titania as photoanode and graphene oxide–CuS composite as a counter electrode material in quantum dot solar cell. *J Mater Res* 2015;30(21):3241–51.
- [17] C HR, Schiffman JD, Balakrishna RG. Quantum dots as fluorescent probes: synthesis, surface chemistry, energy transfer mechanisms, and applications. *Sensor Actuator B Chem* 2018;258:1191–214.
- [18] Khodadadian F, Garza FG, Ommen JR, Stankiewicz AI, Lakervel R. The application of automated feedback and feedforward control to a LED-based photocatalytic reactor. *Chem Eng J* 2019;362:375–82.
- [19] Ahmed SN, Haider W. Heterogeneous photocatalysis and its potential applications in water and wastewater treatment: a review. *Nanotechnology* 2018;29(34):342001.
- [20] Ibhodon A, Fitzpatrick P. Heterogeneous photocatalysis: recent advances and applications. *Catalysts* 2013;3(1):189.
- [21] Beranek R. (Photo)electrochemical methods for the determination of the band edge positions of TiO₂-based nanomaterials. *Adv Phys Chem* 2011;2011:20.
- [22] Yan H, Wang X, Yao M, Yao X. Band structure design of semiconductors for enhanced photocatalytic activity: the case of TiO₂. *Prog Nat Sci Mater Int* 2013;23(4):402–7.
- [23] Klein A. Energy band alignment in chalcogenide thin film solar cells from photoelectron spectroscopy. *J Phys Condens Matter Institute of Phys J* 2015;27(13):134201.
- [24] Saron KMA, Hashim MR, Farrukh MA. Stress control in ZnO films on GaN/Al₂O₃ via wet oxidation of Zn under various temperatures. *Appl Surf Sci* 2012;258(13):5200–5.
- [25] Jilani Asim, Abdel-Wahab MS, Hammad AH. Advance deposition techniques for thin film and coating. *IntechOpen*; 2017.
- [26] Hannachi A, Segura A, Maghraoui-Meherzi H. Growth of manganese sulfide (α -MnS) thin films by thermal vacuum evaporation: structural, morphological and optical properties. *Mater Chem Phys* 2016;181:326–32.

- [27] Hassanien AS, Akl AA. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. *Superlattice Microst* 2016;89:153–69.
- [28] Wang G, Nie Q, Shen X, Chen F, Li J, Zhang W, Xu T, Dai S. Phase change and optical band gap behavior of Ge–Te–Ga thin films prepared by thermal evaporation. *Vacuum* 2012;86(10):1572–5.
- [29] Klenk R, Walter T, Schock HW, Cahen D. A model for the successful growth of polycrystalline films of CuInSe₂ by multisource physical vacuum evaporation. *Adv Mater* 1993;5(2):114–9.
- [30] Merkel JJ, Sontheimer T, Rech B, Becker C. Directional growth and crystallization of silicon thin films prepared by electron-beam evaporation on oblique and textured surfaces. *J Cryst Growth* 2013;367:126–30.
- [31] Mukherjee S, Gall D. Structure zone model for extreme shadowing conditions. *Thin Solid Films* 2013;527:158–63.
- [32] Schulz U, Terry SG, Levi CG. Microstructure and texture of EB-PVD TBCs grown under different rotation modes. *Mater Sci Eng A* 2003;360(1):319–29.
- [33] Yang B, Duan H, Zhou C, Gao Y, Yang J. Ordered nanocolumn-array organic semiconductor thin films with controllable molecular orientation. *Appl Surf Sci* 2013;286:104–8.
- [34] Nakanishi Y, Miyake A, Kominami H, Aoki T, Hatanaka Y, Shimaoka G. Preparation of ZnO thin films for high-resolution field emission display by electron beam evaporation. *Appl Surf Sci* 1999;142(1–4):233–6.
- [35] Meng L, Wang Z, Yang L, Ren W, Liu W, Zhang Z, Yang T, Santos MP. A detailed study on the Fe-doped TiO₂ thin films induced by pulsed laser deposition route. *Appl Surf Sci* 2019;474:211–7.
- [36] Stock F, Antoni F, Diebold L, Gowda CC, Hajjar-Garreau S, Aubel D, Boubiche N, Le Normand F, Muller D. UV laser annealing of Diamond-Like Carbon layers obtained by Pulsed Laser Deposition for optical and photovoltaic applications. *Appl Surf Sci* 2019;464:562–6.
- [37] Prasanth D, Sibin KP, Barshilia HC. Optical properties of sputter deposited nanocrystalline CuO thin films. *Thin Solid Films* 2019;673:78–85.
- [38] Morosanu C, Dumitru V, Cimpoiasu E, Nenu C. Comparison between DC and RF magnetron sputtered aluminum nitride films. In: Prelas MA, Benedictus A, Lin L-TS, Popovici G, Gielisse P, editors. Diamond based composites: and related materials. Dordrecht: Springer Netherlands; 1997. p. 127–32.
- [39] Livage J, Sanchez C, Henry M, Doeuff S. The chemistry of the sol-gel process. *Solid State Ionics* 1989;32:633–8.
- [40] Brook R. Sol-gel technology for thin films, fibers, preforms, electronics and specialty shapes. In: Klein LC, editor. New Jersey, USA: Noyes Publications; 1988. p. 407. bound, US\$72.–ISBN 0-8155-1154-X. *Advanced Materials* 1989, 1 (8–9), 309–309.
- [41] Jian L, Kumar AS, Lekha CSC, Vivek S, Salvado I, Kholkin AL, Nair SS. Strong sub-resonance magnetoelectric coupling in PZT-NiFeO-PZT thin film composite. *Nano-Struct & Nano-Objects* 2019;18:100272.
- [42] Mane RS, Lokhande CD. Chemical deposition method for metal chalcogenide thin films. *Mater Chem Phys* 2000;65(1):1–31.
- [43] (a) Kim S, Choi J. Photoelectrochemical anodization for the preparation of a thick tungsten oxide film. *Electrochim Commun* 2012;17:10–3.
(b) Cristina V, Caramori S, Argazzi R, Meda L, Marra GL, Bignozzi CA. Efficient photoelectrochemical water splitting by anodically grown WO₃ electrodes. *Langmuir* 2011;27(11):7276–84.
- [44] (a) Priyadharsan A, Vasanthakumar V, Shanavas S, Karthikeyan S, Anbarasan PM. Crumpled sheet like graphene based WO₃-Fe₂O₃ nanocomposites for enhanced charge transfer and solar photocatalysts for environmental remediation. *App Surf Sci* 2019;470:114–28.
(b) Kwong WL, Qiu H, Nakaruk A, Koshy P, Sorrell CC. Photoelectrochemical properties of WO₃ thin films prepared by electrodeposition. *Energy Procedia* 2013;34:617–26.
- [45] Shimomura K, Tsurumi T, Ohba Y, Daimon M. Preparation of lead zirconate titanate thin film by hydrothermal method. *Jpn J Appl Phys* 1991;30(9S):2174.
- [46] Takeshi M, Takefumi K, Yutaka Y, Minoru K, Toshiro H. Single process to deposit lead zirconate titanate (PZT) thin film by a hydrothermal method. *Jpn J Appl Phys* 1997;36(5S):2998.
- [47] Urgessa ZN, Oluwafemi OS, Botha JR. Hydrothermal synthesis of ZnO thin films and its electrical characterization. *Mater Lett* 2012;79:266–9.
- [48] Thornton J. Physical vapor deposition. Noyes data corporation, noyes publications, semiconductor materials and process technology handbook for very large scale integration(VLSI) and ultra large scale integration(ULSI). 1988. p. 329–454.
- [49] Westwood W. Physical vapor deposition. In: *Microelectronic materials and processes*. Springer; 1989. p. 133–201.
- [50] Wang X-P, Yu Y, Hu X-F, Gao L. Hydrophilicity of TiO₂ films prepared by liquid phase deposition. *Thin Solid Films* 2000;371(1–2):148–52.
- [51] Koumoto K, Seo S, Sugiyama T, Seo W, Dressick W. Micropatterning of titanium dioxide on self-assembled monolayers using a liquid-phase deposition process. *Chem Mater* 1999;11(9):2305–9.
- [52] Seah MP, Dench W. Quantitative electron spectroscopy of surfaces: a standard data base for electron inelastic mean free paths in solids. *Surf Interface Anal* 1979;1(1):2–11.
- [53] Tanuma S, Powell CJ, Penn DR. Calculations of electron inelastic mean free paths for 31 materials. *Surf Interface Anal* 1988;11(11):577–89.
- [54] Kim J-W, Lee SJ, Biswas P, Lee TI, Myoung J-M. Solution-processed n-ZnO nanorod/p-Co₃O₄ nanoplate heterojunction light-emitting diode. *Appl Surf Sci* 2017;406:192–8.
- [55] Warren BE. *X-ray diffraction*. Courier Corporation; 1969.
- [56] (a) Haefer RA. *Oberflächenmodifikation—ein Überblick*. In: *Oberflächen- und Dünnschicht-Technologie*. Springer; 1991. p. 1–16.
(b) Batra IP. Metallization and metal-semiconductor interfaces, vol. 195. Springer Science & Business Media; 2012.
- [57] Jabłoński A. Über den mechanismus der photolumineszenz von farbstoffphosphoren. *Z Phys* 1935;94(1–2):38–46.
- [58] Jackson M, Mantsch HH. FTIR spectroscopy in the clinical sciences. *Advances in spectroscopy-chichester-john wiley and sons*, vol. 25; 1996. p. 185–216.
- [59] Bell R. *Introductory fourier transform spectroscopy* (New York: academic). 1972.
- [60] Goldstein JI, Newbury DE, Michael JR, Ritchie NW, Scott JHJ, Joy DC. *Scanning electron microscopy and X-ray microanalysis*. Springer; 2017.
- [61] Slade PG. *Electrical contacts: principles and applications*. CRC press; 2017.
- [62] Egerton RF. Applications of energy-loss spectroscopy. In: *Electron energy-loss spectroscopy in the electron microscope*. Springer; 1996. p. 301–402.
- [63] Pennycook SJ, Varela M, Hetherington CJ, Kirkland AI. Materials advances through aberration-corrected electron microscopy. *MRS Bull* 2006;31(1):36–43.

- [64] Giessibl FJ. Advances in atomic force microscopy. *Rev Mod Phys* 2003;75(3):949.
- [65] D'Souza LP, Amoli V, Chandan HR, Sinha AK, Krishna Pai R, Balakrishna GR. Atomic force microscopic study of nanoscale interaction between N719 dye and CdSe quantum dot in hybrid solar cells and their enhanced open circuit potential. *Sol Energy* 2015;116:25–36.
- [66] (a). Islam SZ, Reed A, Wanninayake N, Kim DY, Rankin SE. Remarkable enhancement of photocatalytic water oxidation in N₂/Ar plasma treated, mesoporous TiO₂ films. *J Phys Chem C* 2016;120(26):14069–81.
 (b). Nguyen BH, Nguyen VH. Recent advances in research on plasmonic enhancement of photocatalysis. *Adv Nat Sci Nanosci Nanotechnol* 2015;6(4):043001.
- [67] Shwetharani R, Sakar M, Chandan HR, Geetha Balakrishna R. Observation of simultaneous photocatalytic degradation and hydrogen evolution on the lanthanum modified TiO₂ nanostructures. *Mater Lett* 2018;218:262–5.
- [68] Qing W, Zhengjun Z, Zhengcao L, Qin Z, Yu Z. Enhanced photocatalytic activity of porous α -Fe₂O₃ films prepared by rapid thermal oxidation. *J Phys D Appl Phys* 2008;41(20):202002.
- [69] Tan M, Wang Y, Taguchi A, Abe T, Yang G, Wu M, Tsubaki N. Highly-dispersed Ru nanoparticles sputtered on graphene for hydrogen production. *Int J Hydrogen Energy* 2019;44.
- [70] Huang C-W, Liao C-H, Wu JCS, Liu Y-C, Chang C-L, Wu C-H, Anpo M, Matsuoka M, Takeuchi M. Hydrogen generation from photocatalytic water splitting over TiO₂ thin film prepared by electron beam-induced deposition. *Int J Hydrogen Energy* 2010;35(21):12005–10.
- [71] Dholam R, Patel N, Adami M, Miotello A. Hydrogen production by photocatalytic water-splitting using Cr- or Fe-doped TiO₂ composite thin films photocatalyst. *Int J Hydrogen Energy* 2009;34(13):5337–46.
- [72] Dholam R, Patel N, Adami M, Miotello A. Physically and chemically synthesized TiO₂ composite thin films for hydrogen production by photocatalytic water splitting. *Int J Hydrogen Energy* 2008;33(23):6896–903.
- [73] Xu K, Chatzitakis A, Vøllestad E, Ruan Q, Tang J, Norby T. Hydrogen from wet air and sunlight in a tandem photoelectrochemical cell. *Int J Hydrogen Energy* 2019;44(2):587–93.
- [74] Carrasco-Jaim OA, Ceballos-Sánchez O, Torres-Martínez LM, Moctezuma E, Gómez-Solís C. Synthesis and characterization of PbS/ZnO thin film for photocatalytic hydrogen production. *J Photochem Photobiol A Chem* 2017;347:98–104.
- [75] Huang C-W, Liao C-H, Wu JCS. Photocatalytic separate evolution of hydrogen and oxygen over highly ordered nanorods and bulk TiO₂ thin films. *Journal of Clean Energy Technologies* 2013;1:5.
- [76] Wang X, Li X-y. Photocatalytic hydrogen generation with simultaneous organic degradation by a visible light-driven CdS/ZnS film catalyst. *Mater Sci Eng, B* 2014;181:86–92.
- [77] Ba X, Yan L-L, Huang S, Yu J, Xia X-J, Yu Y. New way for CO₂ reduction under visible light by a combination of a Cu electrode and semiconductor thin film: Cu₂O conduction type and morphology effect. *J Phys Chem C* 2014;118(42):24467–78.
- [78] Cheng M, Yang S, Chen R, Zhu X, Liao Q, Huang Y. Copper-decorated TiO₂ nanorod thin films in optofluidic planar reactors for efficient photocatalytic reduction of CO₂. *Int J Hydrogen Energy* 2017;42(15):9722–32.
- [79] (a). Cheng M, Yang S, Chen R, Zhu X, Liao Q, Huang Y. Copper-decorated TiO₂ nanorod thin films in optofluidic planar reactors for efficient photocatalytic reduction of CO₂. *Int J Hydrogen Energy* 2017;42(15):9722–32.
 (b). Shoji S, Yin G, Nishikawa M, Atarashi D, Sakai E, Miyauchi M. Photocatalytic reduction of CO₂ by Cu_xO nanocluster loaded SrTiO₃ nanorod thin film. *Chem Phys Lett* 2016;658:309–14.
- [80] Chen Y, Kanan MW. Tin oxide dependence of the CO₂ reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts. *J Am Chem Soc* 2012;134(4):1986–9.
- [81] Jiang YF, Chen YY, Zhang B, Feng YQ, N, La Co-doped TiO₂ for use in low-temperature-based dye-sensitized solar cells. *J Electrochem Soc* 2016;163(10):F1133–8.
- [82] Ruiz AM, Cornet A, Morante JR. Study of La and Cu influence on the growth inhibition and phase transformation of nano-TiO₂ used for gas sensors. *Sensor Actuator B Chem* 2004;100(1):256–60.
- [83] Meng A, Zhang L, Cheng B, Yu J. TiO₂–MnOx–Pt hybrid multiheterojunction film photocatalyst with enhanced photocatalytic CO₂-reduction activity. *ACS Appl Mater Interfaces* 2018;11.
- [84] Arconada N, D A, Suárez B, Portela b R, Coronado b JM, Sánchez b B, Castro Y. Synthesis and photocatalytic properties of dense and porous TiO₂-anatase thin films prepared by sol-gel. *Appl Catal B Environ* 2009;86:1–7.
- [85] Baradaran M, Ghodsi F, Bittencourt C, Llobet E. The role of Al concentration on improving the photocatalytic performance of nanostructured ZnO/ZnO: Al/ZnO multilayer thin films. *J Alloy Comp* 2019;788.
- [86] Sakthivel S, Shankar MV, Palanichamy M, Arabindoo B, Bahnemann DW, Murugesan V. Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au, and Pd deposited on TiO₂ catalyst. *Water Res* 2004;38(13):3001–8.
- [87] Jung Jong Min, Wang M, Kim Eui Jung, Park Chinho, Hahn Sung Hong. Enhanced photocatalytic activity of Au-buffered TiO₂ thin films prepared by radio frequency magnetron sputtering. *Appl Catal B Environ* 2008;84:389–92.
- [88] Seong SG, Kim EJ, Kim YS, Lee KE, Hahn SH. Influence of deposition atmosphere on photocatalytic activity of TiO₂/SiO₂ double-layers prepared by RF magnetron sputtering. *Appl Surf Sci* 2009;256(1):1–5.
- [89] Di Mauro A, Fragalà ME, Privitera V, Impellizzeri G. ZnO for application in photocatalysis: from thin films to nanostructures. *Mater Sci Semicond Process* 2017;69:44–51.
- [90] Thickness dependent on photocatalytic activity of hematite thin films. *Int J Photoenergy* 2012;2012.
- [91] Schultz AM, Salvador PA, Rohrer GS. Enhanced photochemical activity of [small alpha]-Fe₂O₃ films supported on SrTiO₃ substrates under visible light illumination. *Chem Commun* 2012;48(14):2012–4.
- [92] Kawahara T, Yamada K-i, Tada H. Visible light photocatalytic decomposition of 2-naphthol by anodic-biased α -Fe₂O₃ film. *J Colloid Interface Sci* 2006;294(2):504–7.
- [93] Mishra M, Chun D-M. α -Fe₂O₃ as a photocatalytic material: a review. *Appl Catal Gen* 2015;498:126–41.
- [94] Bhachu DS, Sathasivam S, Carmalt CJ, Parkin IP. PbO-modified TiO₂ thin films: a route to visible light photocatalysts. *Langmuir* 2014;30(2):624–30.
- [95] Sunada K, Watanabe T, Hashimoto K. Studies on photokilling of bacteria on TiO₂ thin film. *J Photochem Photobiol A Chem* 2003;156(1):227–33.
- [96] (a). Feng Y, Liu L, Zhang J, Aslan H, Dong M. Photoactive antimicrobial nanomaterials. *J Mater Chem B* 2017;5(44):8631–52.
 (b). Wang WJ, Yu JC, Wong PK. Photocatalysts for solar-induced water disinfection: new developments and opportunities. *Mater Sci Forum* 2013;734:63–89.
- [97] Barajas-Ledesma E, García-Benjume M, Espitia-Cabrera I, Bravo-Patino A, Espinoza-Beltrán F, Mostaghimi J,

- Contreras-García M. Photocatalytic activity of Al_2O_3 -doped TiO_2 thin films activated with visible light on the bacteria *Escherichia coli*. *Mater Sci Eng, B* 2010;174(1–3):74–9.
- [98] Barajas-Ledesma E, García-Benjume ML, Espitia-Cabrera I, Bravo-Patiño A, Espinoza-Beltrán FJ, Mostaghimi J, Contreras-García ME. Photocatalytic activity of Al_2O_3 -doped TiO_2 thin films activated with visible light on the bacteria *Escherichia coli*. *Mater Sci Eng, B* 2010;174(1):74–9.
- [99] Decraene V, Pratten J, Wilson M. Cellulose acetate containing toluidine blue and rose bengal is an effective antimicrobial coating when exposed to white light. *Appl Environ Microbiol* 2006;72(6):4436–9.
- [100] Wong MS, Chu WC, Sun DS, Huang HS, Chen JH, Tsai PJ, Lin NT, Yu MS, Hsu SF, Wang SL, Chang HH. Visible-light-induced bactericidal activity of a nitrogen-doped titanium photocatalyst against human pathogens. *Appl Environ Microbiol* 2006;72(9):6111–6.
- [101] Dunnill CW, Parkin IP. Nitrogen-doped TiO_2 thin films: photocatalytic applications for healthcare environments. *Dalton Trans* 2011;40:1635.
- [102] Özkal C, Venieri D, Gounaki I, Meric S. Assessment of thin-film photocatalysis inactivation of different bacterial indicators and effect on their antibiotic resistance profile. *Appl Catal B Environ* 2019;244:612–9.
- [103] Ubonchonlakate K, Sikong L, Saito F. Photocatalytic disinfection of *P.aeruginosa* bacterial Ag-doped TiO_2 film. *Procedia Engineering* 2012;32:656–62.
- [104] (a). Rtimi S, Kiwi J, Karimi A, Sanjinés R. Innovative $\text{Ti}_{1-x}\text{Nb}_x\text{N}-\text{Ag}$ films inducing bacterial disinfection by visible light/thermal treatment. *ACS Appl Mater Interfaces* 2018;10(14):12021–30.
(b). Reddy KR, Karthik K, Prasad SB, Soni SK, Jeong HM, Raghu AV. Enhanced photocatalytic activity of nanostructured titanium dioxide/polyaniline hybrid photocatalysts. *Polyhedron* 2016;120:169–74.
- [105] Wang Z, Roberts RR, Naterer GF, Gabriel KS. Comparison of thermochemical, electrolytic, photoelectrolytic and photochemical solar-to-hydrogen production technologies. *Int J Hydrogen Energy* 2012;37:16287–301.
- [106] Licht S. Solar water splitting to generate hydrogen fuel- a photothermal electrochemical analysis. *Int J Hydrogen Energy* 2005;30:459–70.
- [107] Steinfeld A. Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. *Int J Hydrogen Energy* 2002;27:611–9.
- [108] Currao A. Photoelectrochemical water splitting. *Chimia* 2007;61:815–9.
- [109] da Silva Veras Tatiane, Mozer Thiago Simonato, da Costa Rubim Messeder dos Santos Danielle, da Silva Cesar Aldara. Hydrogen: trends, production and characterization of the main process worldwide. *Int J Hydrogen Energy* 2017;42:2018–33.
- [110] Hallenbeck PC, Ghosh D. Advances in fermentative biohydrogen production: the way forward. *Trends Biotechnol* 2009;27(5):287–97.
- [111] Azzar MY, Hussain MA, Abdul-Wahab AK. Development of biohydrogen production by photobiological, fermentation and electrochemical processes: a review. *Renew Sustain Energy Rev* 2014;31:158–73.
- [112] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. *Int J Hydrogen Energy* 2007;32:3797–810.
- [113] Jing D, Guo L, Zhao L, Zhang X, Liu H, Li M, et al. Efficient solar hydrogen production by photocatalytic water splitting: from fundamental study to pilot demonstration. *Int J Hydrogen Energy* 2010;35:7087–97.
- [114] Maeda K, Domen K. Photocatalytic water splitting: recent progress and future challenges. *J Phys Chem Lett* 2010;1:2655–61.