Nanostructured Zinc Oxide for Water Treatment

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Abstract: Environmental pollution and industrialization on a global scale have drawn attention to the vital need for developing new hygienically friendly purification technologies. Existing wastewater treatment technologies demand high capital investment and operation & maintenance cost, and large area. Cost-effective treatment of pollutants requires the transformation of hazardous substances into benign forms and the subsequent development of effective risk management strategies from harmful effects of pollutants that are highly toxic, persistent, and difficult to treat. Application of nanotechnology that results in improved water treatment options might include removal of the finest contaminants from water (< 300 nm) and "smart materials" or "reactive surface coatings" with engineered specificity to a certain pollutant that destroy, transform or immobilize toxic compounds. Nanomaterials have been gaining increasing interest in the area of environmental remediation mainly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties that develop due to size effects. Heterogeneous photocatalytic systems *via* metal oxide semiconductors like TiO_2 and ZnO, are capable of operating effectively and efficiently for waste water treatment which has been discussed along with other nanotechnology routes that can be useful for water treatments. Multifunctional photocatalytic membranes using ZnO nanostructures are considered advantageous over freely suspended nanoparticles due to the ease of its removal from the purified water. A short discussion on the study of charge transfer mechanisms during photocatalytic reactions has also been included.

Keywords: Contamination, photocatalysis, metal oxide, purification.

INTRODUCTION

Many of the current world problems like high chemical contamination in air, water and soil including high carbon compounds, are related to this fast pace of population growth. Current world population is about 6.5 billion and increasing at an alarming rate and is projected to be 9 million by 2050 [1] Efforts to tackle the population related issues has resulted in severe damage to the ecosystem thereby creating health hazards through environmental pollution. Increased demand for more habitation led to large-scale deforestation and decreased agricultural land, lowering the yield. The production level of food grains is of concern as it has been showing a downward trend over the last decade. Further, extensive use of persistent chemical pesticides to boost agriculture production has also adversely affected our eco-system and is known to have contaminated ground water [2, 3]. Similarly, industrialization is leading to increase in per capita consumption of available natural resources. Out of 1,386 million cubic kilometers (km^3) of water on Earth, 97% is saline and 99.7% of the freshwater is trapped in ice caps and glaciers, or found in groundwater (one third). Only about 0.1 million km^3 of water is above ground in lakes, swamps and rivers, and about 13,000 km^3 in the atmosphere [4].

Surface water has not increased for the past 20 years, and simultaneously, groundwater tables have been dropping [5].

Water is a fundamental requirement for life. The availability of fresh water is crucial for life sustaining activities like drinking, cooking, cleaning, agriculture, etc. Nature has its own mechanism for water recycling to provide us with adequate quantity of fresh water with consumable purity level. Modern human activities have however disrupted the balance between the usage and natural purification processes leading to a shortage of potable water. Most of the natural resources of drinking water are found to be contaminated with diverse toxic materials and pathogenic microorganisms [2] 700 million people across the globe face water scarcity, and it is estimated that this problem will touch 1.8 billion people by 2025 [6]. According to a World Health Organization (WHO) report, water borne diseases kill nearly 12 million people every year [7]. About 90% of all diseases occurring in developing countries are related to the consumption of impure water leading to nearly 4 billion reported cases of diseases contracted from water in the world [8]. Worldwide, there are nearly 4 billion reported cases of diseases contracted from water. 'Low carbon water' through artificial methods has therefore become a necessity for the survival of the human race.

Disinfection of drinking water is currently being carried out through physical and chemical techniques like chlorination, ozonation, UV treatment, etc. Each of the conventional water disinfection processes has limitations

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generating concerns about their mass scale application [2, 3, 9, 10]. Advanced nanotechnology offers unprecedented opportunities for progress—defeating poverty, starvation and disease and expanding human capacities. Nanotechnology is defined as the ability to understand, control, and manipulate matter at the level of individual atoms and molecules, as well as at the "supramolecular" level involving clusters of molecules (in the range of about 0.1 to 100 nm), in order to create materials, devices, and systems with fundamentally new properties and functions because of their small structure [11]. Application of nanotechnology that results in improved waste treatment options might include removal of the finest contaminants from water (< 300 nm) and "smart" materials or reactive surface coatings with induced specificity to a certain pollutant that destroy or immobilize toxic compounds and pathogens.

Heterogeneous photocatalysis is currently being considered as a promising technique for water purification in comparison to other conventional methods [2, 3] as it can break up complex long chained organic molecules (normally toxic) into simpler fragments as well as distort cell walls of microbes thereby immobilizing them. Nanotechnology offers lot of promise in the area of water purification owing to large surface to volume ratios offered by nanostructures [12] and the possibility of preparing photocatalytic membranes by growing semiconducting nanostructures on conventional membranes [13, 14]. The use of renewable energy like solar energy in place of fossil fuels can offer an efficient and clean way of water purification in remote locations. A major advantage of the use of antimicrobial nanomaterial like silver (Ag), zinc oxide (ZnO), etc. in water purification is the prospect of developing point-of-use systems [15]. The concept of decentralized water treatment systems is being considered due to deterioration of water quality in old distribution networks and the ever-increasing transportation costs. The importance of membranes in drinking water and waste water treatment systems is gaining importance [16].

Integration of antimicrobial or photocatalytic nanomaterials makes the membranes functional, achieving multiple treatment goals in a single process while minimizing fouling [15]. Attachment of nanomaterials to supports is crucial to minimize loss of nanomaterials, and also to avoid potential impacts of nanomaterials on human health and ecosystems [17, 18].

PHOTOCATALYSIS FOR WATER DECONTAMINATION

Photocatalysis, using nanostructures of metal oxide semiconductors like zinc oxide (ZnO), titania (TiO_2), tungsten oxide (WO_3), zinc stannate (Zn_2SnO_4), etc. can be an attractive way of water purification as it is capable of removing chemical as well as biological contaminants [19-23]. A good photocatalyst should absorb light efficiently preferably in the visible or near UV part of the electro-magnetic spectrum. Sufficient electron vacant states need to be present to inhibit recombination of electron hole pairs upon light exposure. Photocatalysis applications in the agriculture and microbiology are gaining wide spread acceptance and it is important that the photocatalysts should be biologically inert and non-toxic. Nanostructured photo-catalysts offer large surface to volume ratios allowing higher adsorption of the target molecules. Intensive research over the past decade for its implementation in the purification of drinking water can be found in the literature [2, 24-41]. Efficacy of photocatalysis, in the detoxification of a wide range of industrial and agricultural effluents is also well documented [42]. Another interesting aspect of photo-catayisis is the potential utilization of sunlight, which could allow energy efficient treatment in remote locations.

The underlying mechanism of heterogeneous photo-catalysis is schematically represented in Fig. (**1**). It involves a wide band gap semiconductor photocatalyst, which upon irradiation with light of energy higher than the band gap energy of the material, electron-hole pairs (excitons) are
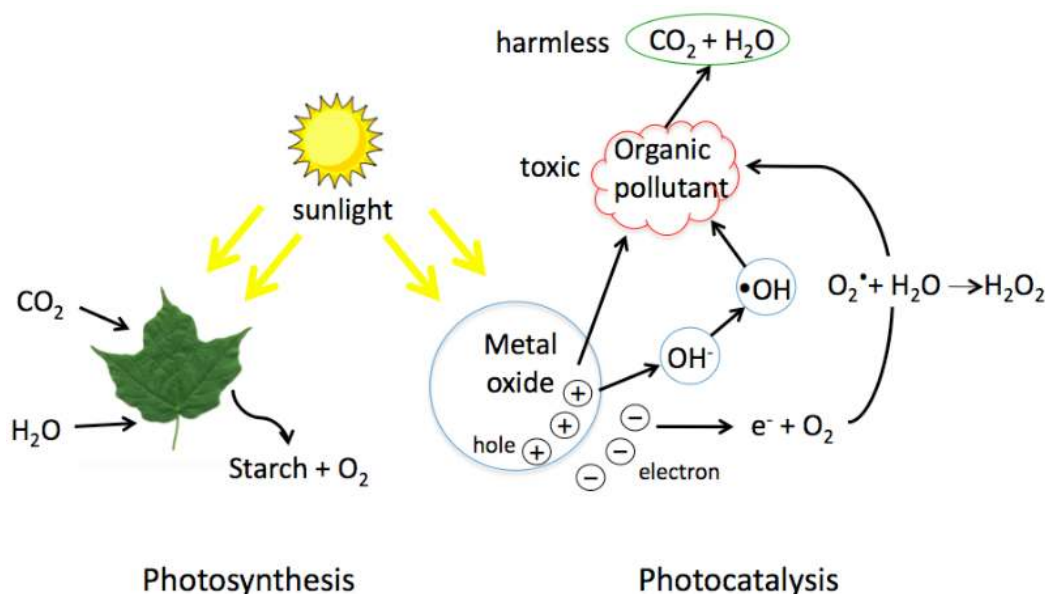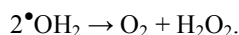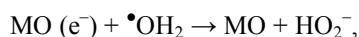

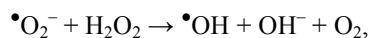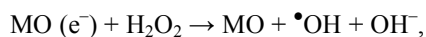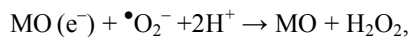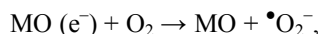**Fig. (1).** Comparison of photosynthesis process in leaves and photocatalysis using metal oxide nanoparticles. In photocatalytic process energy more than the optical bandgap of the semiconductors are generally required (compared to 2.5 eV for photosynthesis process).

created. The photogenerated electron moves up to the conduction band while the hole drifts to the bottom of the valence band. Majority of these photogenerated charge carriers undergo wasteful recombination, while escape recombination and initiate redox reactions in molecules adsorbed at the surface of the photocatalyst and thereby degrading them. The photogenerated electrons and holes have been found to degrade almost all types of organic, inorganic, and microbial contaminants [42], owing to their high redox potentials.
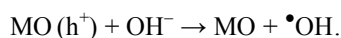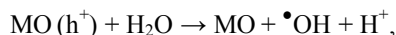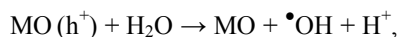
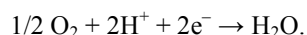The fundamental process during photocatalysis is given by

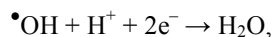$$MO + h\nu \rightarrow MO\ (e^- + h^+)$$
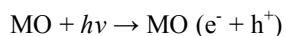
where MO represents a metal oxide photocatalyst like TiO_2, ZnO etc. Photo-generated electrons lead to the formation of superoxide anions ($^\bullet O_2^-$), hydrogenperoxide molecules (H_2O_2), hydroxyl radicals ($^\bullet OH$), hydrogen dioxide anion (HO_2^-) and the hydroperoxy radicals ($^\bullet HO_2$) [19, 43]

$$MO\ (e^-) + O_2 \rightarrow MO + {}^\bullet O_2^-,$$

$$MO\ (e^-) + {}^\bullet O_2^- + 2H^+ \rightarrow MO + H_2O_2,$$

$$MO\ (e^-) + H_2O_2 \rightarrow MO + {}^\bullet OH + OH^-,$$

$${}^\bullet O_2^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- + O_2,$$

$${}^\bullet O_2^- + H^+ \rightarrow {}^\bullet OH_2,$$

$$MO\ (e^-) + {}^\bullet OH_2 \rightarrow MO + HO_2^-,$$

$$HO_2^- + H^+ \rightarrow H_2O_2,$$

$$2{}^\bullet OH_2 \rightarrow O_2 + H_2O_2.$$
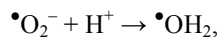
While the oxidation reactions initiated by the photo-generated holes are:

$$MO\ (h^+) + H_2O \rightarrow MO + {}^\bullet OH + H^+,$$

$$MO\ (h^+) + H_2O \rightarrow MO + {}^\bullet OH + H^+,$$

$$MO\ (h^+) + OH^- \rightarrow MO + {}^\bullet OH.$$

The reactions are terminated as:

$${}^\bullet OH + H^+ + 2e^- \rightarrow H_2O,$$

$$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O.$$

Metal oxide nanoparticles show photocatalytic activities. Higher the surface area available, more will be the adsorption of the target molecules and higher will be the efficiency of the photocatalytic reactions. ZnO, with a high surface reactivity owing to large number of active sites, has emerged to be an efficient photocatalyst as compared to TiO_2. The role of oxygen in the photo destruction of organics on catalyst surfaces has been invesitigated as early as in 1991 [44]. Kinetics models were developed to predict the electron uptake by oxygen. The adsorption of oxygen on illuminated photocatalyst surfaces depends on the number of hydroxyl groups of the surface 45. It has also been studied that the dependence of degradation rate constants of organics on the dissolved oxygen concentration can be well described by the Langmuir–Hinshelwood (L–H) equation [46, 47]. ZnO is an attractive material for water treatment as it can be tailored to absorb visible light and is capable of ushering in the era of solar photocatalysis. It has an edge over other metal oxides like TiO_2 in water purification and other

environmental remediation processes as it is soluble in water48 and ends up as metallic zinc in the ecosystem. TiO_2 is however insoluble in water and the nanoparticles can persist in the environment ending up as potential environmental contaminants [19] Further, ZnO can be synthesized under mild conditions and the asymmetry in the crystal structure allows anisotropic growth that can provide large surface to volume ratios [21, 33].

Nanoparticles of metal oxides are efficient photocatalysts and can degrade both chemical and biological contaminants. The biggest limitation in the use of nanoparticles for practical applications is the difficulty of removing the particles after the treatment. It is necessary to granulate the photocatalyst nanoparticles into micron-sized particles (hundreds of microns) or load them onto highly porous substrates, which could be used in various flow-through water treatment facilities to avoid the dispersion of these nanoparticles into the environment and its possible consequences on the environment. The removal of these particles requires expensive post purification through nanofiltration usually together with flocculation and there is serious concern that these particles may ultimately affect the ecosystem. The possible harmful effects of nanoparticles on human health and the eco-system are not yet properly understood. This has necessitated the use of photocatalyst supports, which can be regenerated and can be conveniently removed. It is important to understand how engineered nanomaterials migrate, behave, and interact with living organisms and the abiotic components of the environment, and take proactive steps towards the long-term goal of safer design and disposal of products containing these nanoparticles [49]. For example, the problem related to the removal of ZnO nanoparticles from purified water was addressed by growing ZnO nanorods on various substrates [21, 50-52]. Nanowires consists of a large number of low coordination number atoms at the edge and corner sites of the crystal lattice providing numerous catalytically active sites. Considerable scientific interest is seen for the removal of harmful effects of chemical contaminants from ground-water mainly through photocatalysis using nanoparticles of metal oxide like TiO_2 and ZnO [27, 53].
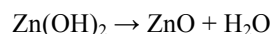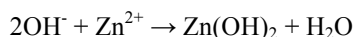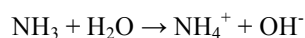
Water purification agents should be capable of removing not only chemical, but also microbial contaminants like bacteria, fungi, virus, molds, etc. Photocatalytic inactivation of microorganisms is a complex process and the rate of inactivation varies with the type, concentration and the physiological state of the microbes [54, 55]. The nature, morphology, concentration, and state (slurry or immobilized) of the catalyst material, also, have a great influence on the microbial inactivation rates [24, 56-58]. Among the various bacterial species, *Escherichia coli* (*E. coli*) which causes diarrhea have been extensively tested to optimize photocatalytic processes as well as for testing newly designed photo reactors [59]. Apart from *E. coli* in pure water, the photocatalytic inactivation of other *coliform bacteria* has also been reported in the literature [60]. TiO_2 nanoparticles (Degussa P25) have been used to successfully inactivate different genera of bacteria including *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhimurium*, and *Enterobacter cloacae* [61]. Reports of photocatalytic inactivation of model microbes like *Escherichia coli*,

Staphylococcus aureus, *Saccharomyces cerevisiae*, and *Aspergilus niger spores* have been reported for palladium (Pd) doped TiO_2 and tin dioxide (SnO_2) films grown on glass substrates [62]. The use of TiO_2 nanoparticles (Degussa P25) to inactivate bacteria (*E. coli, Pseudomonas aeruginosa*), fungi (*Candida albicans, Fusarium sloani*), and protozoa (the trophozoite stage of *Acanthamoebe polyphaga*), spores (*Bacillus subtilis*), and cysts under solar light irradiation are also available in the literature [54].

HYDROTHERMAL GROWTH OF NANOSTRUCTURED ZnO PHOTOCATALYST

Nanostructured ZnO crystals can be synthesized in solution or gaseous phases [21]. The gas phase synthesis methods are complicated involving expensive processes while the solution phase synthesis are normally done under mild conditions in aqueous solvent. The hydrothermal technique of growing ZnO nanostructures has received a lot of attention owing to simple growth conditions. For the synthesis of ZnO nanoparticles, the organometallic process using alcohol as the medium has been widely accepted. This is because of faster nucleation and successive growth in alcoholic solvent as compared to aqueous solvent resulting in well dispersed spherical particles with narrow size distribution [21, 34]. Even though not commonly used, there are scattered reports in the literature on the aqueous synthesis of ZnO nanoparticles [63-65].

The growth of ZnO nanowires on substrates has been an area of intense research for possible applications in areas that require large surface to volume ratios like catalysis, sensing, solar cells, etc. [21, 50, 51, 66] The hydrothermal growth of ZnO nanowires require sources of zinc ions (Zn^{2+}) and hydroxyl ions (OH^-) dissociated in an aqueous solvent [21]. A very commonly used method of growing ZnO nanowires is the use of an equimolar solution of zinc nitrate hexa-hydrate and hexamethylenetetramine (HMT) maintained at temperatures in the range of 65^oC to 95^oC [21, 66]. In order to allow the growth of the nanowires to start from the substrate, a thin film of ZnO nanoparticles is deposited on the substrate through techniques like spin coating, pyrosol, dipping in colloidal solution or dropping and drying. HMT is a non-ionic tetradentate cyclic tertiary amine. HMT, which is highly soluble in water, releases hydroxyl ions through thermal degradation[21]. OH^- ions react with Zn^{2+} ions to form ZnO [67]; the reactions leading to its formation are summarized below:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 + H_2O$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
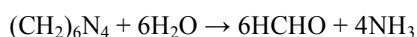
Apart from supplying hydroxyl ions through thermal hydrolysis to drive the precipitation reaction, the role of HMT in the growth of ZnO nanowires has been widely speculated. It is felt that HMT acts as a kinetic buffer as the rate of its hydrolysis decreases with increasing pH and vice versa [50, 68]. In the initial growth stage, the concentration of Zn^{2+} ions (as also the pH) is such that the ZnO growth will be through the formation of $Zn(OH)_2$. With the steady increase in the pH resulting from the decrease in the concentration of the Zn^{2+} ions, $Zn(OH)_2$ becomes thermo-dynamically unstable and the $Zn(OH)_2$ formed start dissolving. Further growth of the nanowires then happen through direct deposition of ZnO [69].

MAKING ZnO VISIBLE LIGHT ACTIVE

In any photocatalytic reactions, apart from factors like type of contaminants and photocatalysts, concentrations, etc., the intensity and wavelength of light irradiation is crucial due to the intrinsic material characteristics [34, 56, 70-72]. TiO_2 and ZnO, which are benchmark UV photocatalysts have very low activity in visible light due to their wide band gaps (above 3 eV) [73, 74]. In order to apply sunlight for photocatalytic degradation of contaminants, the semi-conductors need to be modified by incorporation of transition metals [75-94], semiconductor plasmon coupling [72, 95-101], incorporating nonmetals including co-doping of nonmetals [102-106] or by nanostructure engineering (creating oxygen vacancies and oxygen sub-stoichiometry) [107, 108]. These processes create quasi stable energy states within the band gap facilitating electron hole pair formation at photon energies less than the band gap [33, 34, 109-112]. Visible light photons are then capable of creating excitons leading to photocatalytic reactions. A schematic representation of the energy level and electron transition upon illumination with visible light of doped and undoped ZnO is shown in Fig. (**2**).

A very attractive solution to increase visible light absorption (to facilitate solar photocatalysis) is through the incorporation of crystalline defects in metal oxide semiconductors in the form of vacancies and interstitials. Single crystalline ZnO nanorods has been grown through hydrothermal process [21, 52, 113]. Oxygen vacancies have been introduced in ZnO nanocrystals and has been reported extensively in the literature [33, 34]. Microwave synthesis have been reported for enhancing crystal defects which render the materials photoactive in the visible region [33, 34]. ZnO nanoparticles, nanowires and nanorods prepared through rapid crystallization using microwave assisted hydrolysis showed improved efficiency in photocatalytic degradation of organic dyes [33, 34]. Fig. (**3**) shows the results of the photocatalytic degradation of organic dyes using defect enhanced ZnO nanoparticles and nanorods [33, 36] represented as plots of $ln(C/C_0)$ versus degradation time, where C_0 and C are the initial and final dye concentrations. The defect engineered ZnO nanostructures showed higher degradation efficiencies.

Charge transfer mechanisms during photocatalytic reactions were studied using time correlated single photon count spectroscopy [35] to record the electronic transitions resulting from the de-excitation of the electrons to their stable states. Nanoparticles were excited at a wavelength of 375 nm, instead of deep UV light responsible for band edge transitions. An increase in light absorption in samples prepared through a fast crystallization process can be observed as shown in Fig. (**3b**) inset. The temporal decay of luminescence intensity measured using picosecond spectroscopy with the ZnO nanoparticle samples revealed an excited state lifetime that is multi-exponential as shown in
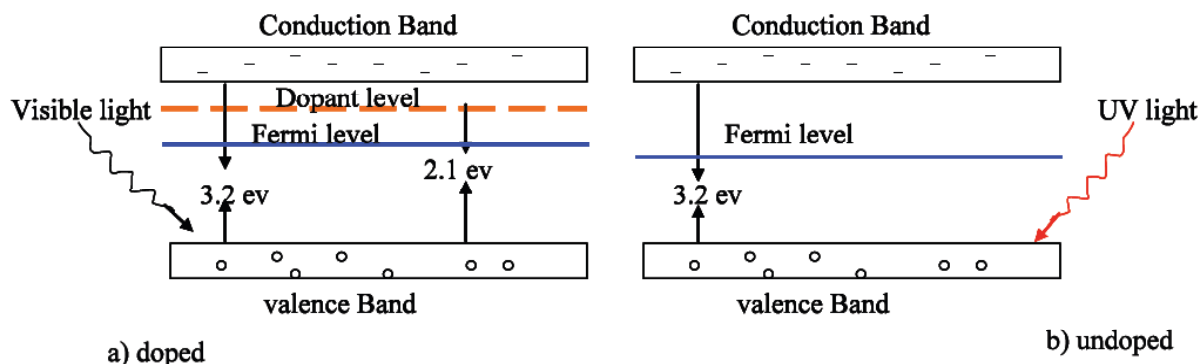
Fig. (2). Schematic diagram of the energy level and electron transition upon illumination with visible light of doped and undoped ZnO.
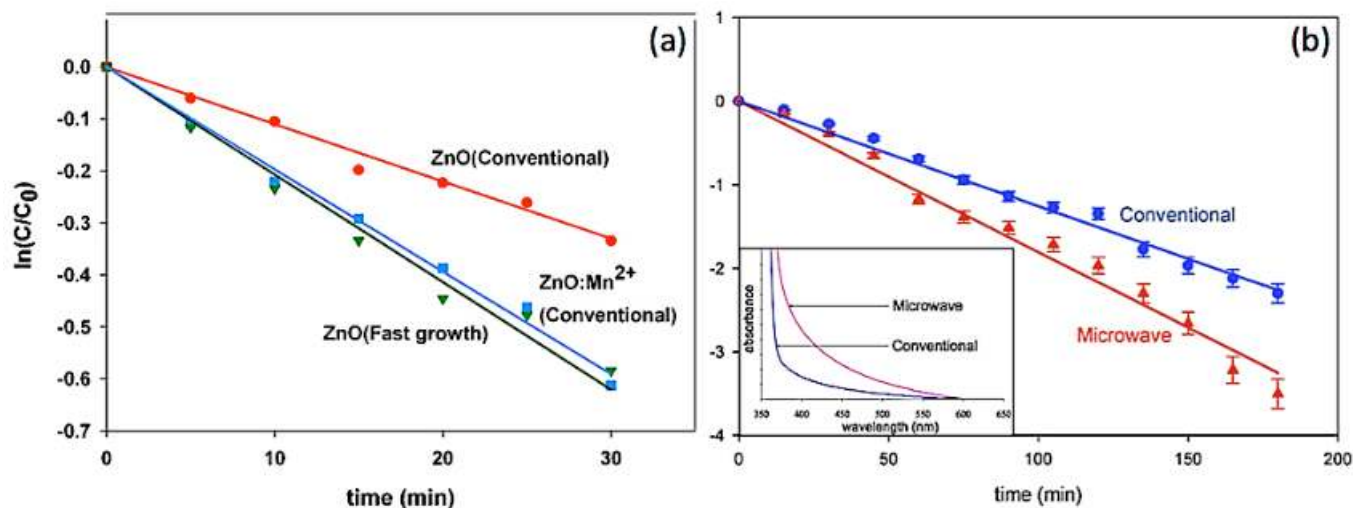

Fig. (3). Photocatalytic decoloration kinetics of a 10 µM aqueous solution of methyelene blue with (**a**) ZnO nanoparticles synthesized through the microwaves assisted fast crystallization technique as well as the pure and Mn-doped ZnO nanoparticles synthesized through the conventional way of slow crystallization process; the photocatalyst samples were used in the slurry forms, illuminated with 22 klux visible light. The degradation rate constants corresponding to the conventionally hydrolyzed undoped and Mn-doped as well as rapidly grown nanoparticles are 0.0110 min^{-1}, 0.0197 min^{-1}, and 0.0207 min^{-1}, respectively (Reproduced with permission from [36]) (**b**) ZnO nanorods synthesized using conventional and fast crystallization methods (comparable effective surface areas). Inset: UV-vis optical absorption spectra of ZnO nanorods grown using conventional hydrothermal method and through microwave irradiation of comparable exposed surface area (Reproduced with permission from [33]).

Fig. (**4a** and **4b**). The lifetime values (τ_i) of the systems was attributed to the transitions from the excitation band to the valence band and/or the coupled singly or doubly charged defect states. The slower component arises from the electrons transiting from electronic defects or electron deficient states to recombine with holes in the valence band. A much faster initial decay in luminescence in the fast-crystallized particles result from higher surface defects compared to what is observed in conventionally hydrolyzed ZnO samples.

MULTI-FUNCTIONAL MEMBRANES

Nanoparticles have found increasing application for water purification but one of its biggest limitations is the difficulty in removing them after the completion of the purification process. This necessitates the use of photocatalyst materials affixed firmly onto supports that can be removed at ease or can be regenerated locally [16, 114-

116]. Photocatalytic membrane reactors (PMRs) have been demonstrated in which photocatalysis was coupled to a filtration process using membranes 116. The membrane played both the role of a simple barrier for the photocatalyst and a selective barrier for the molecules to be degraded [117]. In the PMRs, the catalyst are affixed to the membrane (photocatalytic membranes) or suspended in the reaction mixture. Inclusion of semiconducting nanomaterials renders the membranes functionally active instead of simply providing a diffusion barrier for particulate contaminants [15]. Attachment of nanomaterials to membrane supports is crucial to minimize their loss into the purified water as it may have potential impacts on the ecosystem and human health [17, 18].

A majority of the reports on photocatalytic membranes available in the literature used nanoparticles of either TiO$_2$ or ZnO deposited on conventionally used ceramic or polymer membranes [114, 117-132]. However, for nanomaterials
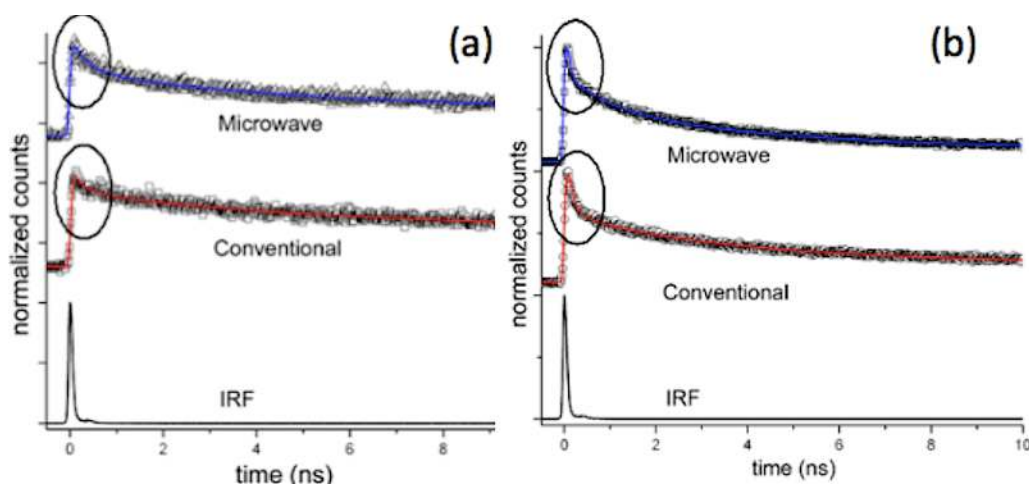
Fig. (4). (**a**) Fluorescence transients observed at 560 nm for conventional and 570 nm for microwave synthesized ZnO nanoparticles (**b**) Fluorescence transients observed at 560nm for conventional and 570 nm for microwave synthesized ZnO nanoparticles in presence of methylene blue (MB) (Reproduced with permission from [35]).

deposited on substrates, one-dimensional nanostructures like nanowires and nanorods offer more effective surface area as compared to nanoparticles [33]. ZnO nanorods are surface independent and they can be grown on any type of membranes through proper surface treatment [14, 133]. Our group has successfully grown ZnO nanorods on a wide variety of membranes made from polymers (polyethylene, polypropylene, etc) [14], glass [38, 50, 51], metals (zinc, aluminium, stainless steel, etc), cellulose based materials like paper [13] and other natural fibers such as cotton [134]. ZnO nanoparticles are affixed on the membranes following a surface treatment as per the materials with which the membranes are made. These seed nanoparticles are then converted into ZnO nanowires/nanorods through a c-axis oriented anisotropic crystal growth in a hydrothermal environment [21, 51]. Very good bonding of the nanoparticles were reported by treating the polymer substrates with thiol followed by immersion in to a colloidal solution of ZnO nanoparticles over extended periods 14. Silanes like amino-propyl trimethoxy silane also proved to be good binders for the nanoparticles in case of metal substrates [135, 136]. Materials with hydroxyl groups like cellulose can easily bind ZnO nanoparticles through possibly hydrogen bondings and do not require any type of surface treatments [13, 134]. Fig. (**5a**) shows scanning electron microscope (SEM) image of ZnO nanorods grown on polyethylene fibers [14] and the four panels in Fig. (**5b**) show various micrographs in a clockwise direction of porous structure of the paper hand sheet, ZnO nanorods growing in the pores, close up view of the ZnO nanorods and ZnO nanorods on the top surface of the paper [13].

ANTIMICROBIAL ACTIVITY OF ZnO

ZnO nanorods were used to degrade model organic dyes like methylene blue and methyl orange as chemical test contaminants and for the inactivation of Gram negative and Gram positive bacteria (*Escherichia coli, Bacillus subtilis and Staphylococcus aureus*) as biological test contaminants [13, 33, 38]. It was observed that ZnO nanorods could effectively degrade dyes like methylene blue and methyl

orange (representatives for long chained organic molecules) [13, 33]. Fig. (**6**) shows comparative photocatalytic activity of ZnO nanoparticulate film and ZnO nanorods of different dimensions [33]. Three nanorod samples of different effective surface areas were used: Sample 1~34.27 cm^2, Sample 2~47.54 cm^2, Sample 3~39.12 cm^2, Nanoparticles ~ 6 cm^2. Owing to higher effective surface area of nanorod arrays, higher degradation rates could be observed compared to the nanoparticulate film of the same substrate size.

Inactivation of gram-negative bacteria *Escherichia coli* and gram-positive bacteria *Bacillus subtilis* in aqueous matrix by ZnO nanorods mediated visible light photocatalysis has also been reported [38, 137-140]. The concentration of Zn^{2+} ions in the aqueous matrix, bacterial cell membrane damage, and DNA degradation were observed after illumination [38]. The inactivation efficiencies for both organisms under illuminated conditions were almost double that under dark conditions. Anomalies in supernatant Zn^{2+} concentration were observed under both conditions as compared to control treatments, while cell membrane damage and DNA degradation were observed only under illumination. Inactivation in the dark was attributed to the bactericidal effect of Zn^{2+} ions, while inactivation under illuminated conditions was primarily due to photocatalytic electron injection process. The inactivation of pathogenic bacterial densities by the ZnO nanorods in the presence of visible light implies potential ex situ application under sunlight for water decontamination at ambient conditions. The levels of dissolved ZnO post-catalysis were determined to be non-lethal [141, 142]. The degree of cell membrane damage among the test organisms was measured using a novel technique based on endonuclease pre-treatment, where evidence of possible DNA damage was also found. Representative electrophoregrams of genomic DNA extracted from endonuclease non-treated or treated cells in the dark or under light exposures to ZnO nanorods are shown in Fig. (**7**) [38].

ZnO nanorods grown on paper prepared from cellulose show antibacterial activity and bactericidal effects were reported [13]. Zone of inhibition (absence of viable bacterial cells) upon illumination with visible light is indicative of
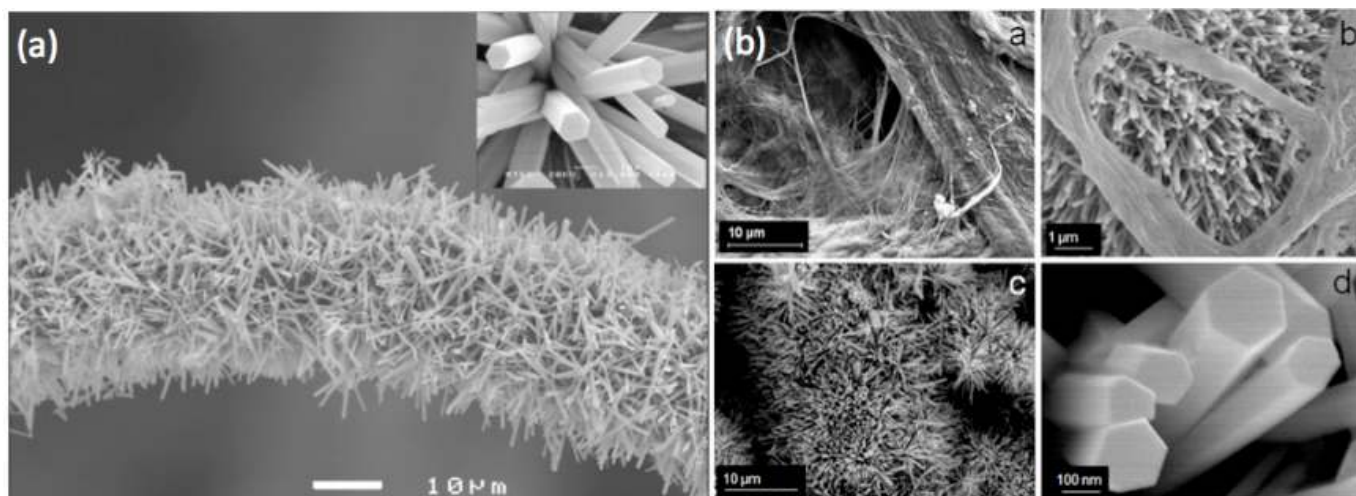
Fig. (5). (**a**) SEM micrograph of ZnO nanorods grown on polyethylene fibers. Inset: magnified image of the nanorods (Reproduced with permission from [14]) (**b**) scanning electron micrographs of **a**. porous structure of the paper hand sheet **b**. ZnO nanorods growing in the pores **c**. ZnO nanorods on the top surface of the paper **d**. close up view of the ZnO nanorods (Reproduced with permission from [13]).

Fig. (6). Photocatalytic degradation of methylene blue using ZnO nanoparticles and nanorods on glass substrates upon excitation with light from a tungsten halogen lamp (~72 klux) (Reproduced with permission from [33]).

Fig. (7). contd….

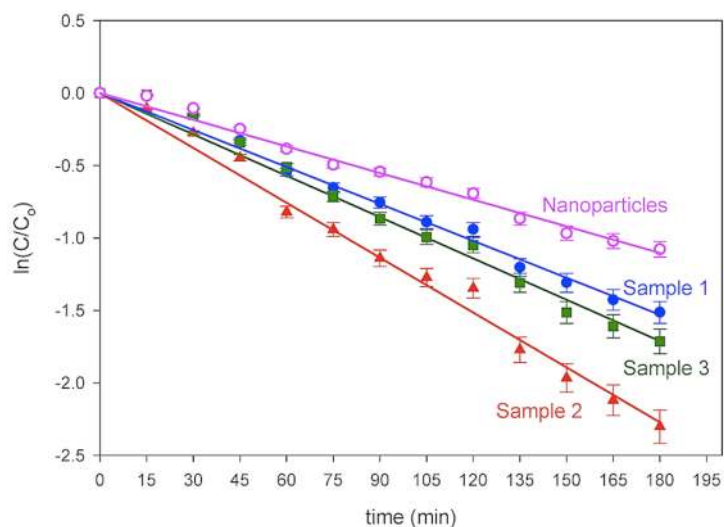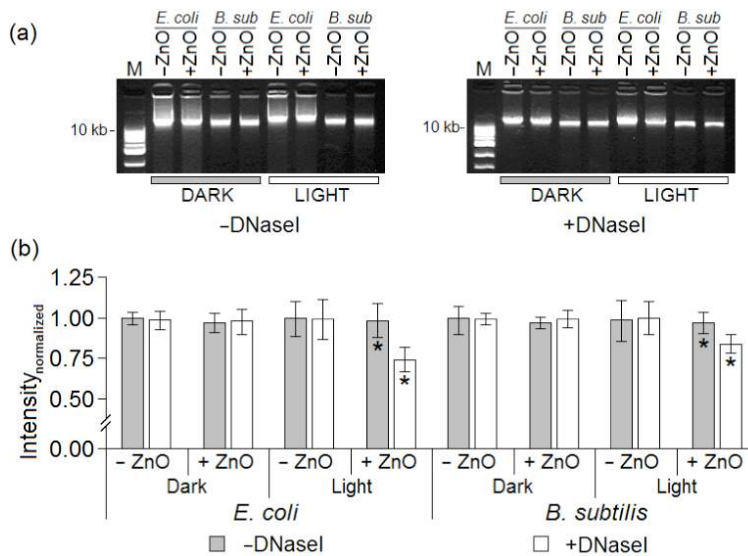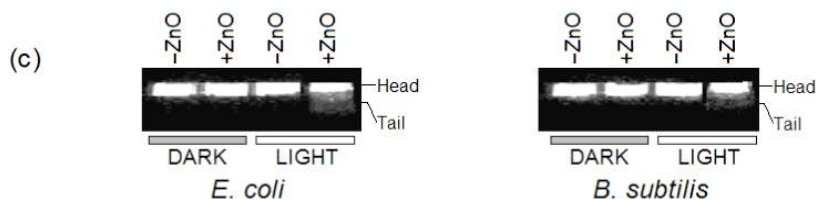**Fig. (7).** Visualization of genomic DNA damage in model organisms induced by ZnO mediated visible light photocatalysis. (**a**) Representative electrophoregrams of genomic DNA extracted from endonuclease non-treated or treated cells following dark or light exposures to ZnO nanorods. (**b**) Average signals (A260) from double-stranded DNA, normalized between endonuclease non-treated and treated pairs. (**c**) Representative electrophoregrams of genomic DNA after the modified comet assay (Reproduced with permission from [38]).

photocatalytic immobilization. It was observed that the bacteria get immobilized on the surface of the photocatalytic paper and also could not flourish in the vicinity of the ZnO treated paper. Fig. (**8**) shows the results of the antibacterial experiments. Photocatalytic paper can be an attractive functional membrane for application in water purification.

PHOTOCATALYSIS IN ACTION

Water Purifier

Inactivation of waterborne bacteria like *Escherichia coli* (*E. coli*), *Bacillus subtilis* (*B. subtilis*) and *Staphylococcus aureus* (*S. aureus*) by ZnO nanorods mediated visible light photocatalysis has been studied [38]. The inactivation efficiencies for both organisms under illuminated conditions were almost double that under dark conditions. Anomalies in supernatant Zn^{2+} concentration were observed under both conditions as compared to control treatments, while cell membrane damage and DNA degradation were observed only under illumination. Inactivation in the dark was attributed to the bactericidal effect of Zn^{2+} ions, while under

illuminated conditions the inactivation is alleviated due to photocatalytic electron injection process. The Zn^{2+} ions released through dissolution binds to the tip of pili of bacteria and prolong the lag phase of the bacterial growth cycle thereby checking reproduction. Strong radicals generated through photocatalysis can disrupt bacterial cell walls creating permanent damage.

The inactivation of pathogenic bacterial densities by the ZnO nanorods in the presence of visible light implies potential ex situ application under sunlight for water decontamination at ambient conditions. The levels of dissolved ZnO post-catalysis were determined to be non-lethal. The degree of cell membrane damage among the test organisms was measured using a novel technique based on endonuclease pre-treatment, where evidence of possible DNA damage was also found [38].

An antibacterial water purifier developed using ZnO nanorods grown on polyethylene fibers is shown in Fig. (**9a**). The water purifier was tested on two model bacteria *E. coli* and *S. aureus*. Up to 99% of *E. coli* and *S. aureus* in spiked
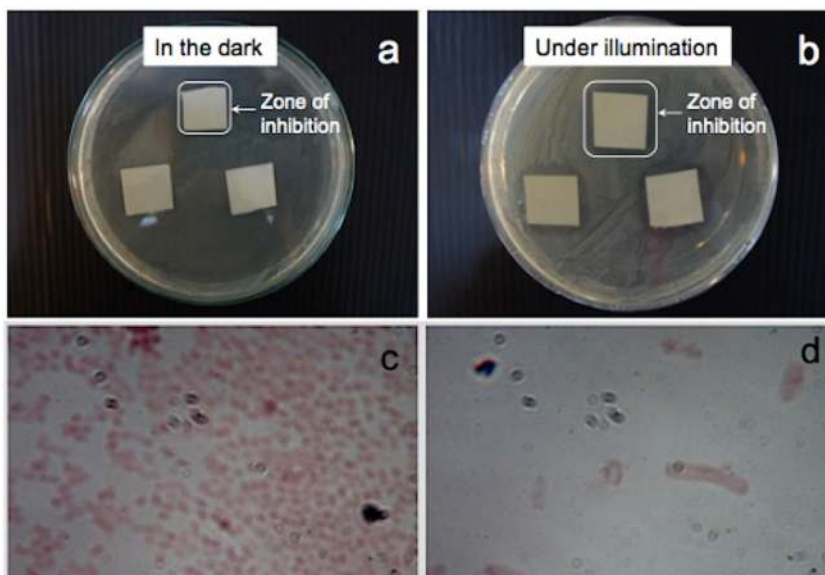
Fig. (8). Results of antibacterial experiments carried out using photocatalytic paper (Sample 1) after incubation for 48 h (**a**) in the dark and (**b**) under illumination with a tungsten halogen lamp. The inhibition zone increased from 1.7×1.7 cm^2 in the dark to 2.1×2.1 cm^2 under visible-light illumination. Optical images taken at a magnification of 1000X (**c**) outside the inhibition zone and (**d**) inside the inhibition zone (Reproduced with permission from [13]).
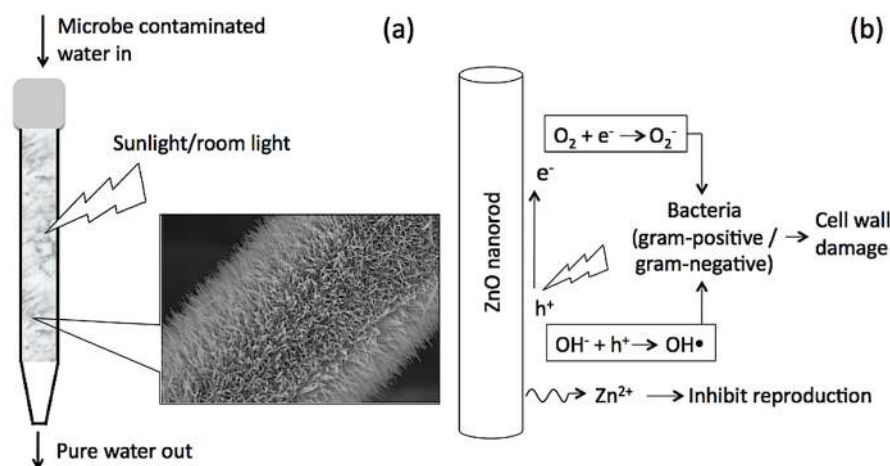
Fig. (9). Schematic representations of (**a**) water purifier comprising of ZnO nanorods on polyethylene fibers enclosed in a glass tube (**b**) mechanism of bacterial immobilization by ZnO nanorods. Free electrons interact with oxygen forming superoxides while the holes convert hydroxyl ions into highly reactive hydroxyl radicals [143] (Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC).

water containing about 10^{10} colony forming units (CFU) of bacterial cells could be immobilized under sunlight, while under room lighting conditions, 80% of *E. coli* and 59% of *S. aureus* cells could be inactivated. This type of water purifiers can be effectively utilized in disaster areas where there is acute scarcity of drinking water and an availability of sunshine. Two mechanisms come play roles in the antibacterial activity of the ZnO nanorods: slow release of zinc ions through dissolution of ZnO and the formation of reactive oxygen species (ROS) through photocatalysis. The mechanism of bacterial inactivation with ZnO nanowires is shown schematically in Fig. (**9b**).

CONCLUSIONS

Technological advancement has severely affected the environment leading to a disparity in the biosphere. Innovative applications of nanotechnology using engineered catalysts exploiting unique properties of nanomaterials are capable of making an impact include the minimization of industrial wastes, sensors to detect toxic molecules in the biosphere. Improved nanostructured photocatalysts are useful for degrading toxic contaminants into benign fragments utilizing solar energy. The concentration of toxic materials and infectious microorganism in the natural resources of drinking water is constantly increasing causing severe environmental pollution. Availability of safe drinking water to people in developing countries has become a serious challenge. Heterogeneous photocatalysis is a promising technique to control environmental pollution whereby toxic organic compounds can be effectively degraded into harmless fragments through a process called photocatalysis using semiconducting nanostructures. Visible light photocatalysis to utilize solar energy, as visible radiation constitutes a major share (~ 46%) of the solar spectrum compared to UV light (~7 %), is getting increasingly popular. Photocatalysis using visible light has been reported to be possible through doping of semiconductors with transition metals to reduce the effective band gap and seem to be attractive for water treatments. This technology is in its infancy and has a

potential of being applied across the water treatment processes.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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