PHOTOCATALYTIC REMIDIATION WITH TIO_2 AS PHOTOCATALYST: A REVIEW

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ABSTRACT

Titanium dioxide has been extensively used as an effective photocatalyst or as sensing system for water and air purification by using nanotechnology.This review paper highlights the use of semiconductor nanoparticle as photocatalystin advanced oxidation process, for eliminating organic and inorganic contaminants in air and water, in presence of UV excitation, extending the response to visible range. Use of semiconductor-metal nanocomposites for more efficient photocatalytic process has also been discussed. The paper also discuss the technology by which nanotechnology offers far more effective ways of eliminating harmful organic contaminants present in the environment.

Keywords: Photocatalysis, Semiconductor-Metalnanocomposites, Tio_2, Visible Light

I. INTRODUCTION

Nanotechnology has fast spread in recent years thereby leaving a profound impact on economic, environmental, social and military areas. With the advancement in nanotechnology, researchers moved towards molecular nanotechnology(MNT) which aimed at improving product functionality, product design time, manufacturing speed and cost. Some theorists have suggested that molecular manufacturing will bring a rapid advancement in the design and our ability to build nano-tech products at incredibly cheaper price. But with the development of MNT are associated numerous risks including the production of potentially hazardous nanoparticles. A favourable point is that semiconductor nanostructures can also develop smart materials that can sense, prevent and reduce the harmful chemical contaminants in the environment and simultaneously destroy them. Semiconductor nanoparticles are used as catalyst for sensing systems of which TiO_2 nanoparticles have been used extensively to remove organic and inorganic contaminants present in the environment. TiO_2can be used as a photocatalyst for the removal of highly toxic and non-biodegradable pollutants normally present in air and waste water via photocatalysis which is a low temperature, non-energy intensive process for the chemical waste remediation. Fujushima and Honda [1] worked on electrochemical splitting of water over TiO_2 to form H_2 and O_2 which led to the vast opportunities of solar energy conversion by semiconductor. Strong oxidation and reduction power of photoexcited titanium dioxide (TiO_2) led to a significant development in a number of photocatalytic applications.

II. PHOTOCATALYTIC MECHANISM OF TiO_2

TiO_2 exist in three different phases: anatase, rutile and brookite. TiO_2 is chemically inert, thermally stable, non-flammable and non-toxic. The large band-gap energy (3.2 eV for the anatase phase) of TiO_2photocatalyst makes it a clear choice for most of the published photocatalysis work. In a pioneering work of Markham[2], photocatalytic properties of ZnO, $TiO_2$and antimony trioxide were studied under UV irradiation. Charge separation method is more commonly employed whereby semiconductor particles are subjected to bandgap excitation. When $TiO_2$is excited by a photon,with energy greater than its band gap energy, electron in valence band move to conduction band, thereby creating electron-hole pair on the surface of TiO_2 nanoparticle. Because of its larger band gap, only UV light source has been found to be effective in the excitation of electron in TiO_2.

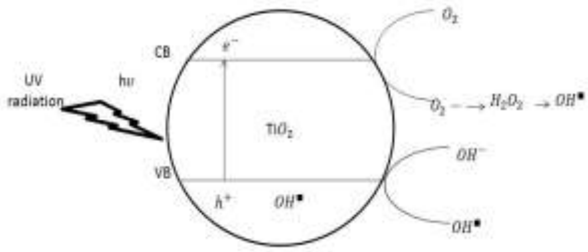

Figure1: Mechanism of Formation of Hydroxyl Radicals and Superoxide Ions under UV Radiation

These excited state electron and holes can react with electron donor and acceptors on the semiconductor surface. After reaction with water, the positive holes form hydroxyl radicals ($OH^{\cdot}$), having strong oxidative decomposing power and react with organic matter. In air, oxygen reduction takes place forming superoxide anions (O_2-). These anions attach to the intermediate products in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then later to water.The hydroxyl ions thus produced or formed play important roles in the photocatalytic reaction mechanism[3-4], depending upon various conditions. In aqueous solutions, the generated OH radicals [5-6] mediate oxidation which is employed largely in the mineralisation of many chemical contaminants. Another approach utilized for charge separation is application of electrochemical bias to a TiO_2 particulate film electrode [7].

III. NANOPARTICLES AS PHOTOCATALYST IN VISIBLE SPECTRAL RANGE

One of the critical limitations of TiO_2 as photocatalyst is its poor response to visible light. In an advancement towards the use of photocatalyst in visible range, the intrinsic properties of a semiconductor is changed in such a way to extend its response in visible region [8-10]. Doping of TiO_2 with transition metal ions resulted in a significant attempt to extend the photoresponse in visible range. Doping of nitrogen into substitutional sites of TiO_2 has shown remarkable phoyocatalytic activity in the visible [11]. Researches have synthesized a photocatalyst that produces stoichiometric amount of oxygen and hydrogen under visible light irradiation [12]. In these classical photocatalyst doping procedures, bandgap reduction approach has been utilised. Significant growth in intermediate band (IB) materials, promises higher efficiencies in photocatalysis allowing light induced degradation of pollutants. IB materials, are semiconductors in which Intermediate band is introduced between CB and VB [13]. On absorption of photons with energy less than bandgap energy E_g, electrons from VB move to the IB and from there to the CB. Using this concept, photons of a wider visible range can be used thus maintaining the same redox capacity. Thus lower energy photons can be used significantly. Several IB materials can be formed by doping semiconductor with transition metals [14]. The materials can be used effectively for degradation of pollutants as well as foe efficient photoevaluation of hydrogen from water. Several research groups have also attempted to utilize the visible light by doping the semiconductor with the sensitizing dye such as Ru (II) polypyridyl complex [15] with an essential requirement of regeneration of oxidised sensitizer to hamper the eventual degradation of sensitizer [16] or by investigating an approach utilizing a tube reactor production based on hollow glass tubes [17]. The experiment suggests coating of glass tubes with TiO_2 and passing UV light through it, resulting in an effective approach towards improving pollutant oxidation.

IV. SEMICONDUCTOR-METAL NANOCOMPOSITES

TiO_2 is considered to be noble photocatalyst due to its low cost, stability and many intrinsic properties but has certain limitations in photocatalytic applications. Its wider bandgap (3.2 eV for anatese) makes it inefficient for visible light utilization thus confining its use to UV light only. To overcome this limitation, techniques such as addition of electron donors, carbonate salts , dye sensitization and metal-ion implantation have been investigated[18]. Several attempts to modify the threshold of UV response of $TiO_2$to visible light response, have lead to possibilities of potential applications. [19-21]. One of the several approaches to enhance the efficiency of photocatalytic reactions is deposition of a noble metal on semiconductor nanoparticles. These noble metals such as gold, silver, platinum [22-23], act by extending the light absorption into the visible range and enhance surface electron excitation by plasmon resonances excited by visible light [18, 21, 22] and modify the surface properties of TiO_2. Nanoparticles of gold and silver, in particular, have been used extensively because of their colour variations in visible region based on plasmon resonance due to collective oscillations of electrons at the surface of nanoparticles. One of the most extensively used chemical methods for doping TiO_2 is sol-gel method. Various other methods proposed to incorporate impurity in TiO_2includes: chemical vapour deposition (CVD), ion-implantation, ion assisted sputtering and plasma. Sol-gel process is one of the easiest methods to prepare nano-size particles. An active dopant is incorporated in the sol during gelation stage which allows direct interaction of doping elements with the support, therefore material acquires photocatalytic properties. Wu et al. [24] proposed two sol-gel methods to prepare vanadium-doped TiO_2photocatalysts. Obtained nano-composite showed higher activity in photodegradation of dyes under visible light than pure TiO_2 [24]. A preparation procedure for doped TiO_2 by sol-gel method requires a dopant precursor, first dissolved in alcohol and then mixed with Titanium precursor, such as titanium isoprooxide(TIP) or titanium tetra chloride. The next step involves hydrolysis which is performed at the room temperature or elevated temperature. The precipitate is then dried at temperature ranging from 80°C to 110°C and later pulverized to obtain xerogel.Calcination is performed in air at temperature ranging from 200 to 600°C. The end result obtained is doped TiO2.Gold nanoparticle- porous TiO_2 composites (Au- TiO_2) have been studied using plasmon induced photoelectrochemistry in visible region. Metal-semiconductor contact results in a favourable charge transfer process leading to efficient photocatalytic reactions. Gold nanoparticles are photoexcited due to plasmon resonance and electrons from excited gold nanoparticles are transferred to TiO_2conduction band. Simultaneous transfer of compensative electrons from donor to the gold nanoparticle takes place. The noble metal are assumed to act as a sink for photoinduced charge carriers to promote charge transfer process. Enhanced photocurrent generation has been observed on gold deposited TiO_2 film in response to visible light irradiation [25-27], but the stability of metal is unknown. Research work carried out by Tetsumaet. al. [28] developed rather stable systems by adding an electron donor and obtained the absorption spectra without applying bias voltage. Au- TiO_2 can be used as a visible-light-sensitive photocatalyst that oxidises ethanol and methanol and reduces oxygen. Silver as a noble metal has resulted in a remarkable improvement in the photoactivity of semiconductor [29, 30]. The Ag nanoparticles (Ag-TiO_2) composite thin films were studied as potential photocatalyst by decoloration mechanism of methylene blue in an aqueous solution. Various studies have suggested that Ag- TiO_2 composite films prepared by sol-gel methods have limited the amount of Ag particles deposited on TiO_2 films because Ag particles tend to coalesc with each other into huge particles during sintering [31]. Also Ag nanoparticles on TiO_2 can be easily oxidised and dissolved in an electrolytic solution under visible light irradiation. To prevent this oxidation, Ag nanoparticles must be coated with SiO_2 shell or Al_2O_3 mask [32]. Composites formed by incorporating Ag and Cu ions into clay minerals/ TiO_2 mixtures with different ratio were capable of effective degradation of ethanol in the visible wavelength range. Another method for Ag- TiO_2 nanocomposite preparation, to overcome the limitationsof mixing in conventional sol-gel method is using molecular precursor method (MPM). This method produces Ag- TiO_2 composite thin films with high concentration of Ag particles and offers excellent miscibility of silver, titaniaprecursor solutions. The absorption spectra obtained for such composite films demonstrated favourable enhancement in photocatalytic reaction rates [33].

V. REMEDIATION OF CONTAMINATED WATER USING NANOPARTICLES

Nanotechnology has provided an improved mechanism for remediation of water and soil over conventional remediation techniques.Ample of ways have been offered by nanotechnology for treating water which is contaminated with dirt, bacteria, viruses, pesticides and heavy metals.Membrane filtering process is also being used by many developing countries to provide clean drinking water. The technique is simple to use and cost effective.Nanofiltersandnanomembranes with specific properties such as pore size and surface reactivityare fabricated which are capable of decontaminating water of organic wastes. Membrane technology allows low cost water treatment with less chemicals and lesser energy consumptions. With the help of membrane technology, water which is contaminated with micro-organism can be processed and converted into drinking water. In the process of reverse osmosis (RO), water is passed through a membrane which is made of crosslinked matrix of polymers and nanoparticles meant to draw water ions and repel contaminants. The pores of membrane are less than 1 nm in diameter which act as tunnel only to water molecules and filter out calcium and sulphate ions. Many industries use iron-powders to clean their industrial wastes because iron, when exposed to contaminants such as trichloroethylene and carbon tetrachloride, break these organic molecules into less toxic carbon compounds. However remediation using iron-powder is not effective and complete in the sense that some chlorinated compounds such as trichloroethylene are only partially treated and toxic byproducts remain even after treatment. Also reactivity of iron powders decrease with time due to the formation of passive layers over the surface of iron granules. Nanotechnology provides a solution to these problems by providing nanoparticles which are 10 to 1000 times more reactive and stable compared to commonly used iron powders[34]. The properties of nanoparticles donot change by soil acidity or temperature thereby maintaining their properties for extended period of time. Nanoscale iron particles effectively transform and detoxify common environmental contaminants without forming any toxic byproducts.

VI. CONCLUSION

Much has been studied and published about nanosized semiconductor oxides acting as photocatalystbecause of their potential effectiveness in providing a solution to environmental problems. Of much importance is the surface area of the photocatalyst where reaction takes place. As the size of the catalyst decreases, the active surface area increases thereby increasing the reaction efficiency. This aspect gives the opportunity to explore one-dimensional nanostructures like nanowires and nanorods to be used for catalysis due to their larger surface-to-volume ratio than nanoparticles. The small sized nanomaterials can allow to develop highly sensitive, pollution monitoring devices.Advancement in technology can help us fabricate nano-sensors which are capable of real-time and continuous monitoring of specific area and produce a digital signal upon detection of specific toxic chemical compounds in water, air, soil or biological systems thus improving current sensing technology. Nano-wires can be used for fabricating real-time sensors that can detect chemical and biological contaminants in food, water and air, leaving a wide area for future developments.

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