Review

Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: A review paper

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Abstract

Various methods to prepare and characterize TiO_2 photocatalyst loaded onto activated carbon (AC) support have been developed over the last decade. This photocatalyst has been used in a variety of investigations, i.e. from water decontamination to direct pollutant degradation in aqueous and gas phase systems using UV irradiation and lately with the assistance of ultrasonic sound waves. Chemical vapor deposition (CVD) method is one of the most promising and well-researched methods for deposition of catalysts onto supports. Given its advantage, from an engineering and fundamental aspect, CVD method also has commercial applications. A detailed search of published reports of these investigations was carried out and analyzed in this paper with focus on CVD techniques, activated carbon support and sonication.
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Keywords: Titanium dioxide; Activated carbon; Chemical vapor deposition; Sonophotocatalysis

Contents

1. Introduction

TiO_2 or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms that are, anatase, rutile, brookite and titanium

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dioxide (B) or TiO$_2$(B). Anatase type TiO$_2$ has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO$_2$ also has a tetragonal crystal structure (with prismatic habit). This type of titania is mainly used as white pigment in paint. Brookite type TiO$_2$ has an orthorhombic crystalline structure. TiO$_2$(B) is a monoclinic mineral and is a relatively newcomer to the titania family. TiO$_2$, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent [1] in toothpastes. The preparation of TiO$_2$ films has even demonstrated futuristic application use such as thin dielectrics in dynamic random access memory (DRAM) storage capacitors [2]. In the last decade, however, TiO$_2$ has been developed and used as a photocatalyst for indoor and outdoor air purification and for the purification and remediation of contaminated waters loaded with low concentrations of toxic organic pollutants [3–6].

1.1. Characteristics of titania photocatalyst

The possible application for this material as a photocatalyst in a commercial scale water treatment facility is due to several factors:

(a) Photocatalytic reaction takes place at room temperature.
(b) Photocatalytic reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products because organic pollutants are usually completely mineralized to non-toxic substances such as CO$_2$, HCl and water (Eq. (7), Table 1) [7–10].
(c) The photocatalyst is inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs), allowing continuous re-use.
(d) Photogenerated holes are extremely oxidizing and photogenerated electrons reduce sufficiently to produce superoxides from dioxygens [11].

In Green Chemistry, researchers [12,13] have also proven that TiO$_2$ can be used to carry out selective photooxidations in non-aqueous systems.

1.2. Mechanism of photocatalytic reaction

The ability to degrade organic and inorganic pollutants comes from the redox environment generated from photo-activation of the TiO$_2$, which is a semiconductor material. The general mechanism of the photocatalytic reaction process on irradiated TiO$_2$ is shown in Table 1. The process of photodegradation of pollutants by TiO$_2$ starts by the absorption of UV radiation equal or higher than the band gap value of 3.2 eV for anatase or 3.0 eV for rutile onto the TiO$_2$ particles. This creates a photogeneration of holes and electron pairs (Eq. (1), Table 1) in the semiconductor valence band (hole) and conduction band (electron). It must be noted that although both anatase and rutile type TiO$_2$ absorb UV radiation, rutile type TiO$_2$ can also absorb radiation that is nearer to visible

light. However, anatase type TiO$_2$ exhibits higher photocatalytic activity than rutile type TiO$_2$ due to its conduction band position which demonstrates stronger reducing power as compared to rutile type TiO$_2$. These energized holes and electrons can either recombine (Eq. (8), Table 1) and dissipate the absorbed energy as heat or be available for use in the redox reactions (Eqs. (2)–(4), Table 1). In the redox reactions, the energized holes and electrons will react with the electron donor or acceptor species adsorbed on the semiconductor surface or simply be nearby in the double layer surrounding the particle [14]. The solid side at the semiconductor/liquid junction creates an electrical field that separates the energized holes/electrons pairs that fail to recombine, allowing the holes to migrate to the illuminated part of the TiO$_2$ and the electrons to migrate to the unlit part of TiO$_2$ particle surface [15]. Basically it is accepted that the initial step for photocatalytic degradation is the formation of extremely reactive but short-lived hydroxyl radical ($^{\bullet}$OH) by hole trapping. The $^{\bullet}$OH is formed either in the highly hydroxylated semiconductor surface or by direct oxidation of the pollutant molecules under UV radiation. There is also a possibility that both methods of forming $^{\bullet}$OH occur in these situations simultaneously. This process is followed immediately by the reduction of adsorbed oxygen species, derived either from dissolved oxygen molecules (in the aqueous system), or by other electron acceptors available in the aqueous system [16].

Although researchers are still studying the complex mechanism involved in the photochemical system, due to the fact that it is a heterogeneous system, commercial applications are available on the market that demonstrate its applicability. On one hand researchers [17–19] have determined that slurry type photocatalytic reactors seem more efficient as compared to those using immobilized catalyst, but actual engineering application often rely on using TiO$_2$ in immobilized form. This is due to several reasons such as the difficulty and cost of catalyst recovering and re-use from a slurry suspension and to functionalization of the support materials which could act as pollutant concentrator thereby speeding-up the purification process. However, photocatalytic purification processes utilizing supported TiO$_2$ are often hindered by other problems such as mass transfer limitations [20,21]. Therefore, due to the complex mechanism that occurs during the photocatalytic reactions and the number of options that exist, it is not simple to determine a common ground for mobilized versus immobilized catalyst performances. However, it is not the intention of this paper to focus on the engineering aspect of the mobility of the supported photocatalyst.

2. Photocatalyst support

TiO$_2$ powder, can by itself, photodegrade pollutant molecules when radiated with UV radiation. If titania powder is deposited in a pool of polluted water under sunlight conditions, it will degrade the pollutant in the water. However, researchers [22] have discovered that during the photodegradation process, interaction by certain pollutant molecules or their intermediates could cause the TiO$_2$ powder to coagulate, thereby reducing the amount of UV radiation from reaching the TiO$_2$ active centers (due to reduction of its surface area) and thus reducing its

Table 1
The general mechanism of the photocatalytic reaction process on irradiated TiO_2

Process	Reaction steps	
Electron-hole pair formation	$TiO_2 + h\nu \rightarrow TiO_2^- + OH^\bullet (orTiO_2^+)$	(1)
(Semiconductor valence band hole and conduction band electron)	$TiO_2^- + O_2 + H^+ \rightarrow TiO_2 + HO_2$	(2)
	$TiO_2^- + H_2O_2 + H^+ \rightarrow TiO_2 + H_2O + OH^\bullet$	(3)
Electron removal from the conduction band	$TiO_2^- + 2H^+ \rightarrow TiO_2 + {}^\bullet H_2$	(4)
Hole trapping	$H^+ + H_2O \rightarrow OH^\bullet + H^+$	(5)
	$H^+ + HO^- \rightarrow OH^\bullet$	(6)
Oxidation of organic pollutant molecules		
	$OH^\bullet + O_2 + C_xO_yH_{(2x-2y+2)} \rightarrow x$ $CO_2 + (x - y + 1)H_2O$	(7)
Non-productive radical reactions		
	$TiO_2^- + OH^\bullet + H^+ \rightarrow TiO_2$ $+ H_2O \text{ (recombination)}$	(8)
	$2OH^\bullet \rightarrow H_2O_2$	(9)
	$2HO_2^- \rightarrow H_2O_2 + O_2$	(10)
	$2OH^\bullet + H_2O_2 \rightarrow H_2O + O_2$	(11)
	$2OH^\bullet + HCO_3^- \rightarrow CO_3^\bullet + H_2O$	(12)

catalytic effectiveness. In order to overcome this coagulation problem, some researchers have used different materials as a support for the titania photocatalyst.

Various substrates have been used as a catalyst support for the photocatalytic degradation of polluted water. For example glass materials: glass mesh, glass fabric, glass wool [23], glass beads [18,24] and glass reactors [19–21,25–32] were very commonly used as a support for titania. Other uncommon materials such as microporous cellulosic membranes [33], alumina clays [34], ceramic membranes [35,36], monoliths [37,38], zeolites [39], and even stainless steel [40] were also experimented as a support for TiO_2. Many more materials were investigated to be used as a support for titania, but only some were mentioned above.

Therefore, from the literature survey we can establish certain underlying criteria for selecting an optimal catalyst support such as:

(a) The supporting material should be transparent or at least allow some UV radiation to pass through it and be chemically inert or non-reactive to the pollutant molecules, its intermediates and the surrounding aqueous system.
(b) The supporting material should sufficiently bond either via physically or chemically to the TiO_2 without reducing the titania's reactivity.
(c) The supporting material should have a high surface area and a strong adsorption affinity towards the pollutants (organic or inorganic compounds) to be degraded. This criterion reduces or eliminates the intermediates produced during the photocatalytic degradation while further increasing mass transfer rates and processes for an efficient photodegradation.

(d) The supporting material should allow for fast and easy photocatalyst recovery and re-use with or without regeneration.

Based on these criteria, activated carbon has also been extensively researched and used as a support material for TiO_2.

2.1. Activated carbon

Activated carbon, which is sometimes called activated charcoal or active carbon, is a porous, amorphous solid carbon material, which is derived mainly from carbonaceous material, such as coal [41] (bituminous, lignite) or plant based (lignocellulosic) material [42–58] such as peat, wood, or nutshells (i.e. coconut, oil palm shells). Generally, the activated carbons are manufactured in two stages that is, carbonization and activation processes [51–58]. The carbonization process, which includes drying and then heating, is done to eliminate by-products such as tars and other hydrocarbons (including volatile organic compounds), from the raw material, as well as to remove any gas produced during this first stage. This pyrolysis process is then completed by heating the material at temperatures between 400 and 600 °C in an oxygen-deficient, inert [51–55] or self-generated [56–58] atmosphere that prevents combustion of the carbonizing material. The carbonized material is then activated in the second stage by exposing them to an activating agent, such as steam [59] or CO_2 [51–55] at the same or higher temperature than that of the first stage. More by-products from the first stage are further burned off by the activation gas during this process, producing a highly porous, three-dimensional graphite lattice structure [60] material that has an exceptionally high surface area. Generally 1 g of activated carbon will have a surface area of between 500 and 2000 m^2, which is typically determined by nitrogen

gas adsorption or a simple liquid adsorption, calculated using Langmuir isotherm for monolayer adsorption or BET (Brunauer, Emmett and Teller) isotherm for multilayer adsorption. The applications for this material are due to its naturally high surface area; although some researchers have used chemical treatment to tailor-make the carbon for very specific applications.

2.2. Activated carbon supported photocatalyst

Activated carbons have also been extensively researched to be used as a support [22,61–65,67–71,79–100] for the TiO_2 photocatalyst including 182 scientific papers and 1341 patents (SCOPUS July 2007), e.g. Ref. [72]. Besides being used as a catalyst support, some researchers use a combination of TiO_2 and activated carbon mixtures to treat pollutant. Some of these studies are listed in Table 2. However, greater understanding of the supported catalyst dispersion in aqueous medium, anchorage and the ideal TiO_2 particle size; mounted on the activated carbon is crucial in developing a suitably supported photocatalyst. Using activated carbon as a catalyst support will help increase the photodegradation rate by progressively allowing an increased quantity of substrate to come in contact with the TiO_2 through means of adsorption. This is important because researchers [73] have established that the oxidizing species (•OH) generated by the photocatalyst, does not migrate very far from the active centers of the TiO_2 and therefore degradation takes place virtually on the catalyst surface. In this respect, activated carbon will prove to be an invaluable support in promoting the photocatalytic process [74–77] in providing a synergistic effect by creating a common interface between both the activated carbon phase and the TiO_2 particle phase. The synergistic effect can be explained as an enhanced adsorption of the target pollutant onto the activated carbon phase followed closely by a transfer through an interphase to the TiO_2 phase, giving a complete photodegradation process.

Therefore from the literature survey, we can establish some benefits of the activated carbon support in the preparation of the titania photocatalyst such as:

(a) Higher activated carbon content in the supported photocatalyst translates to a higher surface area for the supported photocatalyst and higher adsorption capacity.
(b) Activated carbon's pore volume reduction [65] is directly proportionate to its amount in the catalyst, indicating that the TiO_2 particles actually agglomerate on the carbon surface without being adsorbed into the carbon's pores. But pore trappings may still occur to a small extent.
(c) Activated carbon content of less than 13% [65] of the supported photocatalyst weight will create a homogeneous distribution of TiO_2 on its surface. Heterogeneous distribution will occur if the percentage of the carbon is higher than the 13% mentioned, causing both the activated carbon and the TiO_2 particles to form conglomerates.
(d) Organic compounds are hydrophobic whereas TiO_2 particles, when exposed to UV radiation, are hydrophilic. Using activated carbons as a photocatalyst support will help bring the pollutant molecules near to the TiO_2 active site (to come in contact with the hydroxyl radicals) for an efficient and effective photodegradation process (synergistic effect). Activated carbons can generate new adsorption centers to favor approaching pollutant molecules.
(e) Using activated carbon as a support will enable secondary degradation of intermediates to take place in situ, further enhancing the effectiveness of the photocatalyst.
(f) Using activated carbon as a support, allows for fast and easy photocatalyst recovery as well as provide ample room for catalyst regeneration using various techniques [75]. This is because the supported photocatalyst can be made into granular form, hence providing an easy filtering option for recovery from the slurry [78].

Besides having all the criteria and benefits for a catalyst support as established in the literature survey, activated carbon is non-polar, non-reactive, highly adsorptive and cheap to manufacture or purchase.

3. Preparation techniques of loading TiO_2 onto catalyst supports

In order to deposit titania onto a suitable catalyst support, researchers have investigated and developed various techniques and methods. Numerous techniques such as anodization [101], electrodeposition [102], sol–gel [68,70–71], reactive dc magnetron sputtering [103], chemical vapor deposition (CVD) [61–64,66,79–80,104–106], electrostatic sol-spray deposition [107] and aerosol pyrolysis [108] were used for preparing supported titania catalysts. The process of selecting a suitable deposition method depends on the type of catalyst support, the type of pollutant to be degraded, and the degradation environment, for example liquid or gas environment. This is because loading the titania catalyst onto a support can have a profound and irreversible effect on the photocatalytic properties of TiO_2. The catalyst activity and active sites can be affected, to some level, quite severely, by several factors that occur when the catalyst is loaded onto a support. Alteration of the titania's chemical and physical structure including its microcrystalline structure (due to the temperature of preparing the supported titania) plus the chemical bond formed between the support and the titania particles, can drastically change the TiO_2 energy band gap. This energy band determines the effectiveness of the catalyst in producing hydroxyl radicals in an aqueous system. Catalyst surface area reduction due particle bonding with the support and the loss of some titania particles in pore trappings of some types of support (for example, activated carbon), where UV radiation cannot reach, is also a cause for concern. However, the degradation ability of the titania particles trapped in the support's pore can still be effectively exploited by using sonication. This will be explained in the last section of this paper.

In summary, there are two main routes for the preparation of a supported photocatalyst. In the first route, a previously made titania powder is manipulated to procure coating of a suitable support material and in the second route an 'in situ' supported catalyst generation is used. In this paper we shall review this sec-

Table 2
Some of the latest works on TiO$_2$/AC mixture/composite with photocatalyst/sonophotocatalyst combinations and the targeted pollutants

References	TiO$_2$/AC coupling	Preparation method	Degradation method	Pollutant degraded	Comments
[61–62,79]	Composite	MOCVD	Lamp-type (300 W) UV-A	Methyl Orange	HNO$_3$ modified AC effectively increased surface TiO$_2$ particle conc. giving higher catalytic performance.
[63]	Composite	MOCVD, direct air-hydrolysis and high-temperature impregnation techniques	–	–	CVD gave more thermally stable anatase TiO$_2$ than direct air-hydrolysis or high-temperature impregnation technique prepared on AC support.
[64]	Composite	MOCVD	Lamp-type (8 W) UV-A	Phenol	Introducing water vapor during CVD or adsorbing water before CVD was vital for anatase TiO$_2$ deposition on supports. High surface hydroxyl groups and macroporous surface area crucial for coating and photocatalytic reactions.
[65]	Mechanical mixture	–	–	–	AC supports exerts a synergistic effect in combination with TiO$_2$ and modifies catalyst characteristics.
[67]	Composite	Epoxy resin calcinations	Lamp-type (500 W) UV-A	b-Cyclodextrin	Larger pores on the composite photocatalyst are vital for higher adsorption and degradation reaction rates of the targeted pollutants. The composite pore size must be suitable for the corresponding pollutant molecule size.
[68]	Composite	Sol–gel	Lamp-type (40 W) UV range unspecified	Methyl Orange	Higher calcination temperature causes higher crystalline rutile TiO$_2$ to form on the AC support.
[69]	Composite	Carbon precursors calcinations	Lamp-type (2 lamps 20 W each) UV-A	Methylene Blue	Carbon coating technique reduces anatase to rutile transition, allowing for higher temperature annealing process.
[70]	Composite	Sol–gel	Lamp-type (6 lamps 20 W each) UV range unspecified	Phenol	Surface area and porosity of photocatalyst changed drastically due to pollutant adsorption.
[71,99]	Composite	Sol–gel	Sonication (20 kHz, 75 W)	Phenol	Under sonication process, amount of catalyst is proportionate to the degradation rate.
[80]	Composite	MOCVD	Visible light (LED)	NO$_x$ oxidation	High photocatalytic degradation under visible light illumination.
[81]	Hybrid mixture	–	Lamp-type (3 lamps 8 W each) UV-C	Metsulfuron-methyl	Pollutant was flowed through AC column before being photocatalyzed. This hybrid system had a 90% removal rate within 10 min and a high degree of flexibility in system operation.
[82]	Composite	Sol–gel	Lamp-type (20 W) UV-A	Methylene Blue	Sonication was use as means of sample dispersion
[83]	Mechanical mixture	–	Lamp-type (125 W) UV-A	4-Chlorophenol	Synergistic effect observed. Increase of H-type AC's electronic density contributed to titania's photoactivity.
[84]	Composite	Hydrothermal method	Lamp-type (8 W) UV-A	Phenol, Methyl Orange, Cr(IV)	This method provide for low deactivation and easy separation of supported photocatalyst.
[85]	Composite	Acid-catalyzed hydrolysis in NH$_3$ atmosphere	Lamp-type (380 W) Vis (8 W) UV-A	Phenol	Composite (doped N) extended the light absorbance edge to 500–560 nm allowing generation of electron–hole pairs under Vis irradiation.
[86]	Composite	Sol–gel	Microwave (900 W): electrodeless discharge lamp (EDL) UV-A, B, C range	Phenol	EDL largely accelerated the photoreactions causing a relatively faster and effective degradation of phenol.
[87]	Composite	Sol–gel	Lamp-type UV range unspecified	Methylene Blue	Titania was dip-coated on AC fiber showed retained anatase crystalline pattern.

Table 2 (*Continued*)

References	TiO₂/AC coupling	Preparation method	Degradation method	Pollutant degraded	Comments
[88]	Composite	Microwave-assisted digestion	–	–	This method provides fast preparation of photocatalyst as ashing step was not required, chemicals and sample size were reduce and can be treated simultaneously.
[90]	Composite	Epoxy resin calcinations	Lamp-type (500 W) UV-A	Paper mill wastewater	Provided fast and efficient degradation of pollutant (COD), however overuse of catalyst had opposite effects.
[91]	Composite	Aqueous suspension	Lamp-type (60 W) and 4 (15 W) fluorescent tubes UV-A	Catechol, resorcinol	Presence of activated carbon in the photocatalyst enhances the compound interaction and degradation mechanism.
[92]	Composite	Hydrothermal method	Lamp-type (8 W) UV range unspecified	Indigo carmine dye	Increasing the photocatalyst increases the degradation rate but addition of surplus catalyst reduces the rate due to reduction of light penetration.
[93]	Composite	Sol–gel	Lamp-type (3 W) UV-C	Chromotrope 2R	Results indicated that calcinations at 450 °C caused the titania agglomerations in the AC pores enhancing metal oxide and carbon interactions leading to synergistic effect and high photocatalytic ability.
[96]	Mechanical mixture	–	Lamp-type (125 W) UV-A	Phenol, hydroquinone *para*-benzoquinone	Synergistic effect observed, effectively degraded the pollutants
[97]	Composite	Aqueous suspension	Lamp-type (150 W): UV range unspecified (50 W): visible light	Phenol, benzoic acid	TiO_2 was treated with 2,4,6-triphenylpyrilium hydrogen sulfate before mixing with AC, increasing the photocatalyst sensitization to visible light.
[100]	Composite	Sol–gel (sonochemical method)	Lamp-type (15 W) UV-A	Acetone	Slow hydrolysis under sonication promotes the formation of monodispersed TiO_2 sol particles, which agglomerates producing mesoporous TiO_2 particles with narrow pore size distribution.

ond route, giving importance to the chemical vapor deposition method.

3.1. Chemical vapor deposition

Chemical vapor deposition is mainly an industrial chemical process, which uses various deposition techniques to form thin films from different precursors onto a substrate (usually for semiconductor materials). In essence, in a CVD process, a substrate is exposed to a single or multi component volatile precursor (in gaseous phase) in an inert atmosphere at controlled high temperature and pressure. These volatile precursors will either react or decompose onto the surface of the substrate, creating a desired deposited thin-filmed material. Usually by-products are also generated during this process and will be removed by flowing gas through the reactor. In the semiconductor industry, this technique is used in the fabrication process to deposit films such as SiO_2, silicon (polycrystalline, amorphous and expitaxial), silicon–germanium, silicon nitride, titanium nitride, carbon (fiber, filaments and nanotubes), tungsten and various other materials [109–115].

3.2. Metal-organic chemical vapor deposition (MOCVD)

The type of CVD technique used will depend on both the type of substrate and precursors used as well as the desired degree of thin film uniformity. The liquid or gas phase of the precursor is also taken into account when choosing a CVD technique. In preparing TiO_2 photocatalyst supported on activated carbon using CVD method, most researchers [61–62,79,104] choose MOCVD. This preference is due to the metallo-(organic/inorganic) precursors used such as titanium tetra-isopropoxide (TTIP), tetrabutyltitanate (TBOT), titanium tetrachloride or tetranitratotitanium and the activated carbon support. The schematic diagram of a basic MOCVD system is shown in Fig. 1. The carrier gas (for example, N_2) is used to transport the vaporized precursor to the activated carbon support, while at the same time maintaining an inert atmosphere at a specific pressure. The flow pressure generated from the carrier gas is also important in removing gasses generated from the deposition reaction. This is important to prevent 'in situ' generated gasses from causing uneven film uniformity during the decomposition process on the support. Silica gel is used to ensure
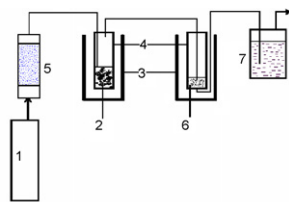
Fig. 1. Schematic diagram of MOCVD system: (1) carrier gas; (2) precursor; (3) vertical tubular furnaces; (4) quartz reactors; (5) silica gel; (6) catalyst support (AC); (7) cold trap.

that the carrier gas is 99.9% dry. This is important because some precursor becomes unstable when wet such as TTIP. The vertical tubular furnaces are used to maintain a specific reaction temperature for vaporizing the precursor and the deposition reaction. The exhaust gasses and 'extra' precursor vapors are removed via a cold trap. The cold trap apparatus can be as simple as flowing the gasses through a beaker of water, allowing almost 90% of the exhaust gasses to dissolve in it.

3.3. Titania deposited on activated carbon support via MOCVD technique

The purpose of using the MOCVD system is to eliminate various steps used in the traditional method of supported photocatalyst preparation such as drying, calcinations and reductions, which can seriously affect catalyst performance. The MOCVD system also provides certain benefits such as the ability to control the titania crystal structure and growth on the support. The process is continuous with relative ease in controlling reaction pressure and temperature, plus a relatively low-cost and simple apparatus is needed for this technique. Catalysts prepared by MOCVD technique have demonstrated higher catalytic efficiency in the degradation of phenol in aqueous system than the two-step method [62,78]. Various benefits can be derived by using this technique in preparing a photocatalyst on activated carbon support such as:

(a) Metallo-organic compounds used as precursors, have relatively low decomposition temperatures and high volatilities, therefore low temperature and pressure are required for the reaction.
(b) Reduction and activation of the catalyst can be carried out simultaneously in the reactor before the catalytic reaction takes place, providing an efficient decomposition reaction; while various unnecessary steps in other traditional techniques are eliminated.
(c) Carrier gas flow rate and source temperature can be adjusted with ease. This is important as researchers have shown that higher flow rate and higher temperature, up to 900 K, will give a higher deposition rate. This is due to the fact that a higher source temperature will create an enhanced concentration of precursor in the gas phase leading to higher deposition rate. However, once the peak temperature has been achieved, the deposition rate will plateau due to limitations of its surface chemical kinetics. Higher deposition temperature, above 1073 K will also cause the percentage of

rutile content to increase, therefore reducing the percentage of anatase content. Other researchers [66], via XRD analysis, have determined that the temperature for anatase to rutile transition depends on the type of precursors and substrates used and is therefore, not the sole effect of temperature. This phenomenon is known as the source effect. Nevertheless a high source temperature of about 448 K, creates better dispersion of the supported titania with fine particle sizes ranging from 10 to 20 nm. Researchers [62] also reported that MOCVD process did not affect the structure and texture of the catalyst support.

4. Sonication and photocatalytic reactions

During deposition process in preparing an activated carbon supported photocatalyst, some titania particles get trapped in the pores of the carbon. This phenomenon is known as 'pore trapping' and UV radiation is blocked by these carbon particles which are unfortunately opaque unlike glass support. This problem somewhat limits the catalytic efficiency to the surface of the carbon particle with the exception to the adsorptive powers of the activated carbon (to remove the organic pollutant from the aqueous system). However, in the last 5 years, researchers [71,116–120] started experimenting with a combination of UV and ultrasonic irradiation processes to enhance the effectiveness of the supported photocatalyst. It was discovered that ultrasonic irradiation can be used as an alternative energy source for TiO_2 to generate positive holes. Sonication of water results in the formation and collapse of millions of microscopic bubbles. When these bubbles collapse, extreme localized high temperature is generated; producing hydroxyl radicals. Nevertheless, researchers [71,99] have determined that with the presence of TiO_2, the hydroxyl concentration is increased and the degradation process takes a shorter time to complete. Also UV irradiation may not be able to penetrate the opaque carbon walls but ultrasonic waves will propagate throughout the entire reactor, thus the shielding effect is no longer a cause for concern even in high particle concentration slurry. Therefore sonication process allows researchers to increase particle concentration in the photocatalytic reactor. In summary, from the literature survey, we can establish some benefits of using sonophotocatalytic degradation process in treating pollutants in an aqueous system such as:

(a) Pore trappings from loading or depositing titania onto opaque substrate, no longer reduces photocatalyst efficiency.
(b) UV irradiation obstructed by high particle concentration slurry can be overcome by using sonication process.
(c) Irradiation intensity (UV and ultrasonic) can be adjusted with ease to optimize the sonophotocatalytic reaction.
(d) The synergy effect of UV and ultrasonic irradiation used in waste water treatment will enable more high energy hydroxyl radicals to be generated, further complementing the adsorptive powers of the activated carbon support to adsorb and degrade the generated intermediate by-products.

(e) Researchers [118,120] have also determined that the positive effect of sonication, influence both the oxidation and reduction reaction processes of the targeted pollutant. But some pollutant may exhibit temperature dependence for an efficient degradation process.

(f) Researchers [22] have demonstrated that sonication as means of stirring as compared to mechanical stirring was effective in preventing coagulation of the photocatalyst.

5. Conclusion

In conclusion, titania photocatalyst supported on activated carbon by means of chemical vapor deposition, appears to have various benefits and advantages for providing a cheap and effective waste water treatment and remediation option. The high surface area, large pores (macroporosity) and the presence of surface hydroxyl groups, makes activated carbon, an ideal photocatalyst support. However, it might be important to note that while certain metallo-organic precursors such as TTIP [64] do not efficiently deposit onto activated carbon support via MOCVD technique, other metallo-(organic/inorganic) precursors may be substituted in order to produce an efficient coating. The use of ultrasonic sound waves in combination with UV irradiation, further contributes to the effectiveness of the activated carbon supported photocatalyst reaction by resolving problems related to the opaque and porous catalyst support. However, numerous aspects and understanding from an engineering point of view still warrant further investigation before large scale commercialization is possible. In our efforts to stem back the tide of environmental degradation, it is only prudent that we continue to explore known technologies and improve our understanding of it.

Acknowledgments

References

[1] G. Meacock, K.D.A. Taylor, M. Knowles, A. Himonides, The improved whitening of minced cod flesh using dispersed titanium dioxide, J. Sci. Food Agric. 73 (2) (1997) 221–225.

[2] S.A. Campbell, H.S. Kim, D.C. Gilmer, B. He, T. Ma, W.L. Gladfelter, Titanium dioxide (TiO_2)-based gate insulators, IBM J. Res. Dev. 43 (3) (1999) 383–392.

[3] D. Ollis, H. Al-Elkabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.

[4] N. Serpone, E. Pellizzetti, Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989.

[5] D. Ollis, E. Pellizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, Environ. Sci. Technol. 25 (9) (1991) 1522–1529.

[6] K.J. Green, R.J. Rudham, Photocatalytic oxidation of propan-2-ol by semiconductor–zeolite composites, J. Chem. Soc., Faraday Trans. 89 (11) (1993) 1867–1870.

[7] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.M. Herrmann, Solar efficiency of a new deposited titania photocatalyst: chlorophenol, pesticide and dye removal applications, Appl. Catal. B 46 (2) (2003) 319–332.

[8] M.A. Aramendia, A. Marinas, J.M. Marinas, J.M. Moreno, F.J. Urbano, Photocatalytic degradation of herbicide fluroxypyr in aqueous suspension of TiO_2, Catal. Today 101 (3-4) (2005) 187–193.

[9] P. Pichat, Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications, Marcel Dekker Inc., New York, Basel, 2003, pp. 77–119.

[10] S. Malato, J. Blanco, A. Compos, J. Caceres, C. Guillard, J.M. Herrmann, A.R. Fernandez-Alba, Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale, Appl. Catal. B 42 (4) (2003) 349–357.

[11] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C 1 (1) (2000) 1–21.

[12] C.E. Taylor, Methane conversion via photocatalytic reactions, Catal. Today 84 (1-2) (2003) 9–15.

[13] K.I. Shimizu, H. Akahane, T. Kodama, Y. Kitayama, Selective photo-oxidation of benzene over transition metal-exchanged BEA zeolite, Appl. Catal. A 269 (1–2) (2004) 75–79.

[14] A.J. Bard, Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors, J. Photochem. 10 (1) (1979) 59–75.

[15] A. Heller, Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells, Acc. Chem. Res. 14 (5) (1981) 154–162.

[16] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, J. Catal. 122 (1) (1990) 178–192.

[17] R. Matthews, S. McEvoy, Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide, J. Photochem. Photobiol. A 64 (2) (1992) 231–246.

[18] M. Bideau, B. Claudel, C. Dubien, L. Faure, H. Kazouan, On the "immobilization" of titanium dioxide in the photocatalytic oxidation of spent waters, J. Photochem. Photobiol. A 91 (2) (1995) 137–144.

[19] G. Chester, M. Anderson, H. Read, S. Esplugas, A jacketed annular membrane photocatalytic reactor for wastewater treatment: degradation of formic acid and atrazine, J. Photochem. Photobiol. A 71 (3) (1993) 291–297.

[20] C. Turchi, D. Ollis, Comment, Photocatalytic reactor design: an example of mass-transfer limitations with an immobilized catalyst, J. Phys. Chem. 92 (23) (1998) 6852–6853.

[21] R. Matthews, Response to the comment. Photocatalytic reactor design: an example of mass-transfer limitations with an immobilized catalyst, J. Phys. Chem. 92 (23) (1998) 6853–6854.

[22] K.E. O'Shea, E. Pernas, J. Saiers, The influence of mineralization products on the coagulation of TiO_2 photocatalyst, Langmuir 15 (6) (1999) 2071–2076.

[23] R. Matthews, Solar-electric water purification using photocatalytic oxidation with TiO_2 as a stationary phase, Solar Energy 38 (6) (1987) 405–413.

[24] N. Serpone, E. Borgarello, R. Harris, P. Cahill, M. Borgarello, Photocatalysis over TiO_2 supported on a glass substrate, Sol. Energy Mater. 14 (2) (1986) 121–127.

[25] M. Muneer, S.J. Das, V.B. Manilal, A. Haridas, Photocatalytic degradation of waste-water pollutants: titanium dioxide-mediated oxidation of methyl vinyl ketone, J. Photochem. Photobiol. A 63 (1) (1992) 107–114.

[26] J. Sabate, M.A. Anderson, H. Kikkawa, M. Edwards, C.G. Hill, A kinetic study of the photocatalytic degradation of 3-chlorosalicylic acid over TiO_2 membranes supported on glass, J. Catal. 127 (1) (1991) 167–177.

[27] M. Abdullah, G.K.C. Low, R. Matthews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, J. Phys. Chem. 94 (17) (1990) 6820–6825.

[28] J. Sabate, M.A. Anderson, H. Kikkawa, Q. Xu, S. Cervera-March, C.G. Hill, Nature and properties of pure and Nb-doped TiO_2 ceramic membranes affecting the photocatalytic degradation of 3-chlorosalicylic acid as a model of halogenated organic compounds, J. Catal. 134 (1) (1992) 36–46.

[29] V. Brezová, M. Jankovičová, M. Soldán, A. Blažková, M. Reháková, I. Šurina, M. Čeppan, B. Havlínová, Photocatalytic degradation of *p*-toluenesulphonic acid in aqueous systems containing powdered and immobilized titanium dioxide, J. Photochem. Photobiol. A 83 (1) (1994) 69–75.

[30] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, Factors affecting the photocatalytic degradation of dichlorvos over titanium dioxide supported on glass, J. Photochem. Photobiol. A 76 (1–2) (1993) 103–110.

[31] R. Matthews, Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide, J. Catal. 111 (June (2)) (1998) 264–272.

[32] R. Matthews, Photooxidation of organic impurities in water using thin films of titanium dioxide, J. Phys. Chem. 91 (12) (1987) 3328–3333.

[33] I.R. Bellobono, M. Bonardi, L. Castellano, E. Selli, L. Righetto, Degradation of some chloro-aliphatic water contaminants by photocatalytic membranes immobilizing titanium dioxide, J. Photochem. Photobiol. A 67 (1) (1992) 109–115.

[34] K. Kato, Photocatalytic property of TiO$_2$ anchored on porous alumina ceramic support by the alkoxide method, J. Ceram. Soc. Jpn. 101 (3) (1993) 245–249.

[35] M. Anderson, M.J. Gieselmann, Q. Xu, Titania and alumina ceramic membranes, J. Membr. Sci. 39 (3) (1988) 243–258.

[36] S. Tunesi, M. Anderson, Influence of chemisorption on the photodecomposition of salicylic acid and related compounds using suspended titania ceramic membranes, J. Phys. Chem. 95 (8) (1991) 3399–3405.

[37] M. Sauer, D. Ollis, Acetone oxidation in a photocatalytic monolith reactor, J. Catal. 149 (1) (1994) 81–91.

[38] R. Mariscal, J.M. Palacios, M. Galan-Ferreres, J.L.G. Fierro, Incorporation of titania into preshaped silica monolith structures, Appl. Catal. A 116 (1–2) (1994) 205–219.

[39] Y. Xu, H. Langford, Enhanced photoactivity of a titanium (iv) oxide supported on zsm5 and zeolite a at low coverage, J. Phys. Chem. 99 (29) (1995) 11501–11507.

[40] Y.M. Gao, H.S. Shen, K. Dwight, A. Wold, Preparation and photocatalytic properties of titanium (IV) oxide films, Mater. Res. Bull. 27 (9) (1992) 1023–1030.

[41] M. Jagtoyen, M. Thwaites, J. Stencel, B. McEnaney, F. Derbyshire, Adsorbent carbon synthesis from coals by phosphoric acid activation, Carbon 30 (7) (1992) 1089–1096.

[42] Z. Hu, E.F. Vansant, Synthesis and characterization of a controlled-micropore-size carbonaceous adsorbent produced from walnut shell, Microporous Mater. 3 (6) (1995) 603–612.

[43] R. Arriagada, R. Garcia, M. Molina-Sabio, F. Rodriguez-Reinoso, Effect of steam activation on the porosity and chemical nature of activated carbons from *Eucalyptus globulus* and peach stones, Microporous Mater. 8 (3–4) (1997) 123–130.

[44] M.T. Gonzalez, F. Rodriguez-Reinoso, A.N. Garcia, A. Marcilla, CO$_2$ activation of olive stones carbonized under different experimental conditions, Carbon 35 (1) (1997) 159–162.

[45] J.C. González, M.T. González, M. Molina-Sabio, F. Rodríguez-Reinoso, A. Sepulveda-Escribano, Porosity of activated carbons prepared from different lignocellulosic materials, Carbon 33 (8) (1995) 1175–1177.

[46] K. Gergova, S. Eser, Effects of activation method on the pore structure of activated carbons from apricot stones, Carbon 34 (7) (1996) 879–888.

[47] M.Z. Hussein, R.S.H. Tarmizi, Z. Zainal, R. Ibrahim, M. Badri, Preparation and characterization of active carbons from oil palm shells, Carbon 34 (11) (1996) 1447–1449.

[48] I. Abe, M. Hitomi, N. Ikuta, I. Kawafune, Y. Kera, Properties of porous carbons prepared from the wood of Japanese Cypress—effect of carbonization time at 900 °C, Carbon 34 (11) (1996) 1455.

[49] T.T. Al-Khalid, N.M. Haimour, S.A. Sayed, B.A. Akash, Activation of olive-seed waste residue using CO$_2$ in a fluidized-bed reactor, Fuel Process. Technol. 57 (1) (1998) 55–64.

[50] N. Tancredi, T. Cordero, J. Rodriguez-Mirasol, J.J. Rodriguez, Activated carbons from Uruguayan eucalyptus wood, Fuel 75 (15) (1996) 1701–1706.

[51] K. Anuar, A. Halim, Z. Zulkarnain, M.H. Zobir, S. Hamdan, O.S. Wooi, Preparation and characterization of activated carbon from Gelam Wood

(*Melaleuca cajuputi* sp.): surface and porosity studies, Ultra Sci. 12 (3) (2000) 355–360.

[52] K. Anuar, G.J. Collin, B.H.A. Faujan, Z. Zulkarnain, M.H. Zobir, A.A. Halim, Preparation and characterization of activated carbon derived from resak wood (*Vatica hullettii*), Res. J. Chem. Environ. 5 (3) (2001) 21–24.

[53] K. Anuar, G.J. Collin, B.H.A. Faujan, Z. Zulkarnain, M.H. Zobir, A.A. Halim, Preparation and characterization of activated carbon derived from resak wood (*Vatica hullettii*): surface area and porosity studies, Oriental J. Chem. 18 (1) (2002) 43–46.

[54] K. Anuar, G.J. Collin, Z. Zulkarnain, M.H. Zobir, M.J. Haron, A.A. Halim, Surface area and porosity studies of activated carbons prepared from oil palm shells (*Elaeis guineensis*) using physical and chemical activators such as CO$_2$, H$_3$PO$_4$, K$_3$PO$_4$, and KOH, ASEAN J. Sci. Technol. Dev. 20 (2) (2003) 149–158.

[55] K. Anuar, G.J. Collin, Z. Zulkarnain, M.H. Zobir, M.J. Haron, A.A. Halim, Activated carbons prepared from oil palm shells: application for column separation of heavy metals, Indian Chem. Soc. 81 (2004) 1–4.

[56] G.J. Collin, A.A. Fauziah, F.M.Z. Hasnul, F.D. Siti, Treatment of landfill leachate in Kayu Madang, Sabah: porosity and adsorption studies (part 2), Asian Chem. Lett. 10 (3 and 4) (2006) 89–94.

[57] G.J. Collin, Y. Frankie, Textural and chemical characterization of activated carbons prepared from rice husk (*Oryza sativa*) using a two-stage activation process, JESTEC, in press.

[58] G.J. Collin, B. Awang, K. Duduku, S.K. Onn, Sorption studies of methylene blue in aqueous solution by optimized carbon prepared from Guava seeds (*Psidium guajaval*), J. Mater. Sci. 13 (1) (2007) 83–87.

[59] J.P. Boudou, Surface chemistry of a viscose-based activated carbon cloth modified by treatment with ammonia and steam, Carbon 41 (10) (2003) 1955–1963.

[60] A. Oberlin, High-resolution TEM studies of carbonization and graphitization, in: P.A. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 22, Marcel Dekker Inc., New York, 1989.

[61] X. Zhang, M. Zhou, L. Lei, Enhancing the concentration of TiO$_2$ photocatalyst on the external surface of activated carbon by MOCVD, Mater. Res. Bull. 40 (11) (2005) 1899–1904.

[62] X. Zhang, M. Zhou, L. Lei, S. Xu, Synthesis of TiO$_2$ supported on activated carbon by MOCVD: operation parameters study, J. Zhejiang Univ. Sci. 5 (12) (2004) 1548–1553.

[63] A.H. El-Sheikh, A.P. Newman, H. Al-Daffaee, S. Phull, N. Cresswell, S. York, Deposition of anatase on the surface of activated carbon, Surf. Coat. Technol. 187 (2–3) (2004) 284–292.

[64] Z. Ding, X. Hu, P.L. Yue, G.Q. Lu, P.F. Greenfield, Synthesis of anatase TiO$_2$ supported on porous solids by chemical vapor deposition, Catal. Today 68 (1–3) (2001) 173–182.

[65] J. Arana, J.M. Dona-Rodriguez, E.T. Rendon, C.G. iCabo, O. Gonzalez-Diaz, J.A. Herrera-Melian, J. Perez-Pena, G. Colon, J.A. Navio, TiO$_2$ activation by using activated carbon as a support. Part 1: Surface characterization and decantability study, Appl. Catal. B 44 (2) (2003) 161–172.

[66] C. Byun, J.W. Jang, I.T. Kim, K.S. Hong, B.-W. Lee, Anatase-to-rutile transition of titania thin films prepared by MOCVD, Mater. Res. Bull. 32 (4) (1997) 41–440.

[67] R. Yuan, R. Guan, J. Zheng, Effect of the pore size of TiO$_2$-loaded activated carbon fiber on its photocatalytic activity, Scr. Mater. 52 (12) (2005) 1329–1334.

[68] Y. Li, X. Li, J. Li, J. Yin, Photocatalytic degradation of methyl orange by TiO$_2$-coated activated carbon and kinetic study, Water Res. 40 (6) (2006) 1119–1126.

[69] M. Inagaki, F. Kojin, B. Tryba, M. Toyoda, Carbon-coated anatase: the role of the carbon layer for photocatalytic performance, Carbon 43 (8) (2005) 1652–1659.

[70] B. Tryba, A.W. Morawski, M. Inagaki, Application of TiO$_2$-mounted activated carbon to the removal of phenol from water, Appl. Catal. B 41 (4) (2003) 427–433.

[71] M. Kubo, H. Fukuda, X.J. Chua, T. Yonemoto, Kinetics of ultrasonic degradation of phenol in the presence of composite particles of titanium dioxide and activated carbon, Ind. Eng. Chem. Res. 46 (3) (2007) 699–704.

[72] Z. Lin, X. Lin, Environmental-protective and energy-saving carbon felt, Patent No. CN1817633, 16th Aug. 2006.

[73] C. Minero, F. Catozzo, E. Pelizzetti, Role of adsorption in photocatalyzed reactions of organic molecules in aqueous titania suspensions, Langmuir 8 (2) (1992) 481–486.

[74] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, Effect of inert supports for titanium dioxide loading on enhancement of photodecomposition rate of gaseous propionaldehyde, J. Phys. Chem. 99 (24) (1995) 9986–9991.

[75] M. Sheintuch, Y.I. Matatov-Meytal, Comparison of catalytic processes with other regeneration methods of activated carbon, Catal. Today 53 (1) (1999) 73–80.

[76] J. Matos, J. Laine, J. Hermann, Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon, Appl. Catal. B: Environ. 18 (3–4) (1998) 281–291.

[77] J. Herrmann, J. Matos, J. Disdier, C. Guillard, J. Laine, S. Malato, J. Blanco, Solar photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon in aqueous suspension, Catal. Today 54 (2-3) (1999) 255–265.

[78] L. Lei, H.P. Chu, X. Hu, P.L. Yue, Preparation of heterogeneous photocatalyst (TiO₂/alumina) by metallo-organic chemical vapor deposition, Ind. Eng. Chem. Res. 38 (9) (1999) 3381–3385.

[79] X. Zhang, M. Zhou, L. Lei, TiO₂ photocatalyst deposition by MOCVD on activated carbon, Carbon 44 (2) (2006) 325–333.

[80] C. Kuo, Y. Tseng, C. Huang, Y. Li, Carbon-containing nano-titania prepared by chemical vapor deposition and its visible-light-responsive photocatalytic activity, J. Mol. Catal. A 270 (1-2) (2007) 93–100.

[81] N. Areerachakul, S. Vigneswaran, H.H. Ngo, J. Kandasamy, Granular activated carbon (GAC) adsorption-photocatalysis hybrid system in the removal of herbicide from water, Sep. Purif. Technol. 55 (2007) 206–211.

[82] M.L. Chen, C.S. Lim, W.C. Oh, Preparation with different mixing ratios of anatase to activated carbon and their photocatalytic performance, J. Ceram. Process. Res. 8 (2007) 119–124.

[83] T. Cordero, J.-M. Chovelon, C. Duchamp, C. Ferronato, J. Matos, Surface nano-aggregation and photocatalytic activity of TiO₂ on H-type activated carbons, Appl. Catal. B: Environ. 73 (2007) 209–362.

[84] S.X. Liu, X.Y. Chen, X. Chen, A TiO₂/AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method, J. Hazard. Mater. 143 (2007) 257–263.

[85] S. Liu, X. Chen, Preparation and characterization of a novel activated carbon-supported N-doped visible light response photocatalyst (TiO₂-xNy/AC), J. Chem. Technol. Biotechnol. 82 (2007) 453–459.

[86] Y. Liu, S. Yang, J. Hong, C. Sun, Low-temperature preparation and microwave photocatalytic activity study of TiO₂-mounted activated carbon, J. Hazard. Mater. 142 (2007) 208–215.

[87] B.-Y. Jia, L.-Y. Duan, C.-L. Ma, C.-M. Wang, Characterization of TiO₂ loaded on activated carbon fibers and its photocatalytic reactivity, Chin. J. Chem. 25 (2007) 553–557.

[88] A.H. El-Sheikh, J.A. Sweileh, A rapid and simple microwave-assisted digestion procedure for spectrophotometric determination of titanium dioxide photocatalyst on activated carbon, Talanta 71 (2007) 1867–1872.

[89] H. Huang, Y.-K. Du, J.-T. Dai, P. Yang, Preparation of TiO₂/ACF catalysts and their photodegradation on tetrachloroethylene, Ganguang Kexue yu Guanghuaxue/Photographic Sci. Photochem. 25 (2007) 123–129.

[90] R. Yuan, R. Guan, P. Liu, J. Zheng, Photocatalytic treatment of wastewater from paper mill by TiO₂ loaded on activated carbon fibers, Colloids Surf. A 293 (2007) 80–86.

[91] J. Araña, J.M. Doña Rodríguez, O. González Díaz, J.A. Herrera Melián, J. Pérez Peña, The effect of modifying TiO₂ on catechol and resorcinol photocatalytic degradation, J. Solar Energy Eng. 129 (2007) 80–86.

[92] A.K. Subramani, K. Byrappa, S. Ananda, K.M. Lokanatha Rai, C. Ranganathaiah, M. Yoshimura, Photocatalytic degradation of indigo carmine dye using TiO₂ impregnated activated carbon, Bull. Mater. Sci. 30 (2007) 37–41.

[93] W. Wang, C.G. Silva, J.L. Faria, Photocatalytic degradation of Chromotrope 2R using nanocrystalline TiO₂/activate carbon composite catalysts, Appl. Catal. B: Environ. 70 (2007) 470–478.

[94] J.M. Doña, C. Garriga, J. Araña, J. Pérez, G. Colón, M. Macías, J.A. Navio, The effect of dosage on the photocatalytic degradation of organic pollutants, Res. Chem. Intermediates 33 (2007) 351–358.

[95] L.Y. Zou, Y. Luo, E.J. Hu, Using titania photocatalyst to degrade toluene in a combined adsorption and photocatalysis process, J. Adv. Oxid. Technol. 1 (2007) 31–36.

[96] J. Matos, J. Laine, J.-M. Herrmann, D. Uzcategui, J.L. Brito, Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenols photodegradation, Appl. Catal. B: Environ. 70 (2007) 461–469.

[97] H.S. Hilal, L.Z. Majjad, N. Zaatar, A. El-Hamouz, Dye-effect in TiO₂ catalyzed contaminant photo-degradation: sensitization vs. charge-transfer formalism, Solid State Sci. 9 (2007) 9–15.

[98] J.H. Liu, R. Yang, S.M. Li, Preparation and application of efficient TiO₂/ACFs photocatalyst, J. Environ. Sci. 18 (2006) 979–982.

[99] M. Kubo, H. Fukuda, X.J. Chua, T. Yonemoto, Ultrasonic degradation of phenol in the presence of composite particles of TiO₂ and activated carbon, in: AIChE Annual Meeting, Conference Proceedings, 2005, pp. 10358–10360.

[100] Y. Yu, J.C. Yu, J.G. Yu, Y.C. Kwok, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes, Appl. Catal. A: Gen. 289 (2005) 186–196.

[101] J. Pouilleau, D. Devilliers, F. Garrido, S. Durand-Vidal, E. Mahe, Structure and composition of passive titanium oxide films, Mater. Sci. Eng., B, Solid-State Mater. Adv. Technol. 47 (1997) 235–243.

[102] S. Karuppuchamy, K. Nonomura, T. Yoshida, T. Sugiura, H. Minoura, Cathodic electrodeposition of oxide semiconductor thin films and their application to dye-sensitized solar cells, Solid State Ionics 151 (2002) 19–27.

[103] S. Takeda, S. Suzuki, H. Odaka, H. Hosono, Photocatalytic TiO₂ thin film deposited onto glass by DC magnetron sputtering, Thin Solid Films 392 (2001) 338–344.

[104] F.-D. Duminica, F. Maury, F. Senocq, Atmospheric pressure MOCVD of TiO₂ thin films using various reactive gas mixtures, Surf. Coat. Technol. (188–189) (2004) 255–259.

[105] K. Wang, Y. Hsieh, P. Chao, C. Cgang, The photocatalytic degradation of trichloroethane by chemical vapor deposition method prepared titanium dioxide catalyst, J. Hazard. Mater. 95 (2002) 161–174.

[106] G.A. Battiston, R. Gerbasi, A. Gregori, M. Porchia, S. Cattarin, G.A. Rizzi, PECVD of amorphous TiO₂ thin films: effect of growth temperature and plasma gas composition, Thin solid Films 371 (2000) 126–131.

[107] C.H. Chen, E.M. Kelder, J. Schoonman, Electrostatic sol-spray deposition (ESSD) and characterisation of nanostructured TiO₂ thin films, Thin solid Films 342 (1999) 35–41.

[108] L. Kavan, M. Grätzel, Highly efficient semiconducting TiO₂ photo-electrodes prepared by aerosol pyrolysis, Electrochim. Acta 40 (1995) 643–652.

[109] R.E.I. Schropp, B. Stannowski, A.M. Brockhoff, P.A.T.T. van Veenendaal, J.K. Rath, Hot wire CVD of heterogeneous and polycrystalline silicon semiconducting thin films for application in thin film transistors and solar cells, Mater. Phys. Mech. 1 (2) (2000) 73–82.

[110] R.C. Jaeger, Film Deposition, in: Introduction to Microelectronic Fabrication, Modular Series on Solid State Devices, vol. 5, second ed., Prentice Hall, Upper Saddle River, 2002.

[111] D.L. Smith, Thin-Film Deposition: Principles and Practice, McGraw-Hill, 1995.

[112] D.M. Dobkin, M.K. Zuraw, Principles of Chemical Vapor Deposition, Kluwer, 2003.

[113] U. Qureshi, C. Blackman, G. Hyett, I.P. Parkin, Tungsten oxide and tungsten oxide-titania thin films prepared by aerosol-assisted deposition—use of preformed solid nanoparticles, Eur. J. Inorg. Chem. 10 (2007) 1415–2142.

[114] J. Perez-Mariano, K.-H. Lau, A. Sanjurjo, J. Caro, J.M. Prado, C. Colominas, Multilayer coatings by chemical vapor deposition in a fluidized bed

reactor at atmospheric pressure (AP/FBR-CVD): TiN/TaN and TiN/W, Surf. Coat. Technol. 201 (2006) 2174–2180.

[115] M. Zhu, J. Wang, R.A. Outlaw, K. Hou, D.M. Manos, B.C. Holloway, Synthesis of carbon nanosheets and carbon nanotubes by radio frequency plasma enhanced chemical vapor deposition, Diamonds Relat. Mater. 16 (2007) 196–201.

[116] C. Berberidou, I. Poulios, N.P. Xekoukoulotakis, D. Mantzavinos, Sonolytic, photocatalytic and sonophotocatalytic degradation of malachite green in aqueous solutions, Appl. Catal. B 74 (2007) 63–72.

[117] K. Hirano, H. Nitta, K. Sawada, Effect of sonication on the photo-catalytic mineralization of some chlorinated organic compounds, Ultrason. Sonochem. 12 (2005) 271–276.

[118] N.J. Bejarano-Pérez, M.F. Suárez-Herrera, Sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO_2 as a catalyst, Ultrason. Sonochem. 14 (2007) 589–595.

[119] V. Ragaini, E. Selli, C.L. Bianchi, C. Pirola, Sono-photocatalytic degradation of 2-chlorophenol in water: kinetic and energetic comparison with other techniques, Ultrason. Sonochem. 8 (2001) 251–258.

[120] I.Z. Shirgaonkar, A.B. Pandit, Sonophotochemical destruction of aqueous solution of 2,4,6-trichlorophenol, Ultrason. Sonochem. 5 (1998) 53–61.