Review

A review of solar and visible light active TiO$_2$ photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern

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ABSTRACT

Research into the development of solar and visible light active photocatalysts has been significantly increased in recent years due to its wide range of applications in treating contaminants of emerging concern (CECs), endocrine disrupting compounds (EDCs), bacteria and cyanotoxins. Solar photocatalysis is found to be highly effective in treating a wide range of CECs from sources such as pharmaceuticals, steroids, antibiotics, phthalates, disinfectants, pesticides, fragrances (musk), preservatives and additives. Similarly, a number of EDCs including polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), bisphenol A (BPA), organotins (OTs), volatile organic compounds (VOCs), natural and synthetic estrogenic and androgenic chemicals, pesticides, and heavy metals can be removed from contaminated water by using solar photocatalysis. Photocatalysis was also found effective in treating a wide range of bacteria such as *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Salmonella typhi* and *Micrococcus lylae*. The current review also compares the effectiveness of various visible light activated TiO$_2$ photocatalysts for treating these pollutants. Doping or co-doping of TiO$_2$ using nitrogen, nitrogen–silver, sulphur, carbon, copper and also incorporation of graphene nano-sheets are discussed. The use of immobilised TiO$_2$ for improving the photocatalytic activity is also presented. Decorating titania photocatalyst with graphene oxide (GO) is of particular interest due to GO's ability to increase the photocatalytic activity of TiO$_2$. The use GO to increase the photocatalytic activity of TiO$_2$ against microcystin-LR (MC-LR) under UV-A and solar irciation is discussed. The enhanced photocatalytic activity of GO–TiO$_2$ compared to the control material is attributed to the effective inhibition of the electron–hole recombination by controlling the interfacial charge transfer process. It is concluded that there is a critical need for further improvement of the efficiency of these materials if they are to be considered for bulk industrial use.

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1. Introduction

Rigorous investigations of titanium dioxide [1–7] have been carried out ever since Fujishima and Honda discovered its ability to split water using a TiO_2 anode and Pt counter electrode in 1972 [8]. Frank and Bard also highlighted its use as a photocatalyst in the area of water remediation in 1977 [9]. TiO_2 is important in a wide range of commercial applications [10], as a pigment in certain formulations such as paints [11,12], toothpastes and suncreams [13,14] due to its strong white colour and also in various applications such as water splitting [15,16], self-cleaning [17–20], sterilisation [21], anti-fogging [22], lithography [23], degradation of organic compounds [24,25], and metal corrosion prevention [26,27]. Titanium dioxide occurs in nature in three different crystalline forms; anatase, brookite and rutile, with rutile being the most abundant and thermodynamically stable [28]. Yet it is anatase that exists as the most photoactive phase because of its improved charge-carrier mobility and the higher number of surface hydroxyl groups [29]. Photocatalysis is widely stated as the process of using light to activate a substrate (such as a semiconductor photocatalyst), in order to accelerate or facilitate photoreactions but with the catalyst remaining unconsumed [20,30,31]. A photocatalytic reaction is initiated when a photo-excited electron is promoted from the filled valence band (VB) of semiconductor photocatalyst to the empty conduction band (CB) as the absorbed photon energy, $h\nu$, equals or exceeds the band gap of the semiconductor photocatalyst (Fig. 1). This reaction results in leaving behind a positive hole in the valence band and a negative electron in the conduction band, thus creating an electron–hole pair ($e^- – h^+$) [32]. The positive hole in the valence band can oxidize the OH^- or water at the surface to produce hydroxyl radical ($^\bullet OH$) which acts as extremely powerful oxidant of organic pollutants. The photo-excited electron located in the conduction band is reduced to form the superoxide radical anion ($O_2^{\bullet -}$) upon reaction with oxygen and hydroperoxide radical ($^\bullet OOH$) upon further reaction with H^+ [33]. These reactive oxygen species (ROS) are pivotal in the degradation of organic compounds.

Stoichiometric anatase titania is active in the near-UV, limiting its utility to environments with a significant ultraviolet light flux. It is chemically and photo-chemically stable, but having a relatively large band gap of 3.2 eV, it is only activated upon irradiation with photons of light in the UV domain (≥ 387 nm), and thus the light utilization efficiency to solar irradiation and visible light is limited [31]. Of the solar spectrum, only 4–5% is UV light with visible light making up approximately 40%. Therefore, in order to enhance the solar efficiency of TiO_2 under solar irradiation, attempts were made to extend the absorption range of titanium dioxide into the visible-light region [2,34–37]. Some methods used to improve the efficiency of TiO_2 are impurity doping [38,39], sensitisation [40], surface modification [41], and fabrication of composites with other materials [42]. Modified TiO_2 can differ from standard TiO_2 in several ways including light adsorption, charge recombination dynamics, surface structure and charge, interfacial charge transfer kinetics, and adsorption of target pollutants [42]. The role of the dopants in forming the resulting material needs to be considered. The use of cations (usually metals) for the doping of TiO_2 was generally avoided due to their tendency to increase charge carrier recombination centres [29], and the generation of secondary impurity phases which inevitably reduces the photo-activity of titania [43]. It was also suggested that despite the decrease in band gap energy, metals were not always successfully introduced into the TiO_2 framework, and that the remaining metals on the outside surface sheltered the photo-reaction sites [44]. Significant attention has been directed at reducing the band gap and in turn increasing the visible light activity of TiO_2 by doping with a range of non-metal elements
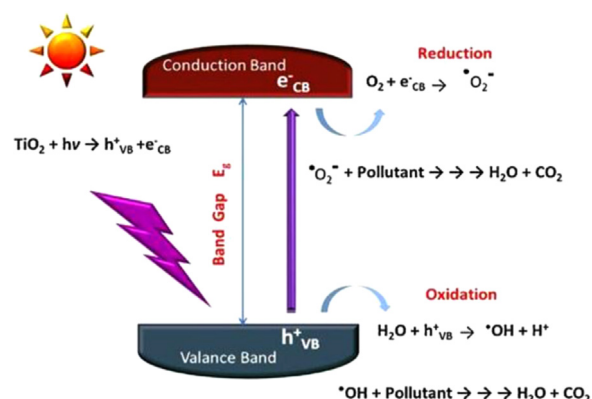

Fig. 1. Schematic illustration of the photocatalytic process. (Banerjee, Dionysiou and Pillai, Appl. Catal. B Environ. 176–177 (2015) 396). Copyright 2015, reprinted with permission from Elsevier.

including nitrogen [34,45–49], carbon [43,50–53], sulphur [54–56], phosphorous [57], boron [58,59], oxygen [60], and fluorine [61,62], along with heterojunctions [63–67] and combinations of these elements [68–73].

2. Advances in the development of visible light active photocatalysts

Noble metals such as Ag [74–76], Au [75–77], Pt [78] and Pd [79] and/or combinations of these metals with each other or other materials have also been studied extensively for their properties and their contribution toward visible light absorption. Ag was of particular interest due to its well-known properties of improving the photocatalytic efficiency under visible light irradiation by acting as an electron trap and delaying the recombination of the electron–hole pair through the promotion of the interfacial charge transfer. Seery et al. reported the enhanced photocatalytic activity with Ag doping of TiO_2 due to the ability of Ag to trap the excited e^-, limiting the recombination rate and thus allowing the generation of more $^\bullet OH$ which results in enhanced photocatalytic ability of the material [80]. Nolan et al. observed that silver nanoparticles exhibit a high level of absorbance in the visible light region (Fig. 2A) and further proposed a mechanism for the visible light absorbance by Ag TiO_2 seen in Fig. 2B below [81]. It has been suggested that it is the surface plasmon resonance of the silver nanoparticles and the surface oxidised Ag that are responsible for the visible light responsiveness of TiO_2. This work also observed that a weakening in the titania bridging complex in the presence of silver encouraged the anatase to rutile transition which, in turn, may affect the photocatalytic activity of the prepared material.

In more recent years, efforts to combine Ag with other materials as composites for use in areas such as water disinfection and self-cleaning cotton textiles have been studied [82–84]. One such material is that of Ag/AgCl [82], which exhibited much higher reactivity under visible light due to the surface plasmon resonance of the Ag-NPs and the production of $Cl^\bullet$ through oxidation of Cl ions by the holes which are themselves reactive radical species capable of oxidising organic pollutants. A composite of Ag–AgI–TiO_2/CNFs [83] was studied by Yu et al. [83]. The combined effect of the plasmon resonance of metallic Ag nanoparticles resulting in visible light responsiveness, the oxidation of the Ag and I (Iodine) resulting in the generation of reactive radical species and the presence of carbon nanofibers (CNFs) contributing to a high absorbance capacity and high conductivity of the composite made this a material of interest in the area of environmental remediation.
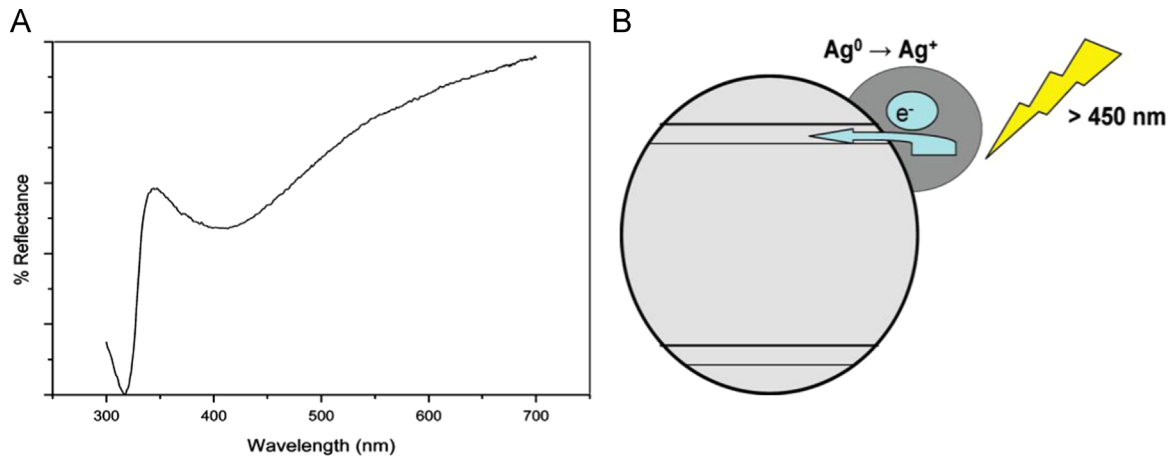
Fig. 2. (A) Diffuse reflectance spectrum of silver nanoparticles b) Schematic diagram showing the mechanism for light absorption of Ag nanoparticles. (Nolan , Seery, Hinder, Healy and Pillai, J. Phys. Chem. C 114 (2010) 13026) reprinted with permission from American Chemical Society.

Due to problems associated with metal doping, non-metal elements were studied comprehensively in the hope of achieving visible light active stable titanium dioxide. Non-metal doping, as mentioned above, has been the subject of extensive analysis with nitrogen, carbon and different non-metal combination systems being of most interest for visible light enhancement [85]. Ever since Sato in 1986 reported visible light responsive activity after the incorporation of nitrogen in a titania precursor sol [86], nitrogen has been seen as the most promising dopant due to the high stability of nitrogen and the comparable atomic sizes of nitrogen and oxygen. Asahi et al. suggested that the effective band gap narrowing was the result of successful doping of nitrogen into substitutional sites due to the mixing of 2p orbitals of N and O [87]. Serpone et al. [88] later suggested that it was the formation of defects associated with oxygen vacancies that was responsible for the visible light activity. Di Valentin et al. [89] studied the effect of nitrogen doping in great detail using density functional theory (DFT) and suggested several routes of nitrogen doping including substitutional and interstitial sites with the generation in discrete energy levels above the valence band often referred as a midgap state. Regardless of the numerous studies based on nitrogen doping, the electronic structure and the exact species responsible for visible light activation of the doped material remains controversial but is found to be dependant on the route of preparation. Carbon was also an element of increased interest over the years with several publications focusing on the electronic structure of carbon doped TiO_2. Etacheri et al. [64] studied carbon doped TiO_2 heterojunctions for antibacterial activity. From their study, XPS analysis was conducted on pure anatase and C-doped TiO_2 to investigate the influence of carbonate impurities on the electron structure of TiO_2. It was seen that the widths of the valence bands of the two materials were equal, pointing to almost similar mobilities of photo-generated charge carriers (Fig. 3A). It was also deduced that the observed visible light activity was due to the formation of localised C 2p interband states of the carbonate ions in the band gap, located approximately 0.26 eV above the valence band (Fig. 3B).

Heterojunction photocatalysts, such as the anatase–rutile system, exhibit characteristics preferential for the production of enhanced visible light activity. These systems promote the effective transfer of photo-excited electrons from the conduction band of anatase to that of rutile and favour electron–hole separation (see Fig. 4). Pillai and co-workers have successfully prepared several anatase–rutile systems doped with non-metals, including nitrogen, a nitrogen and sulphur co-doping system and a carbon doped system resulting in anatase–brookite heterojunction mentioned
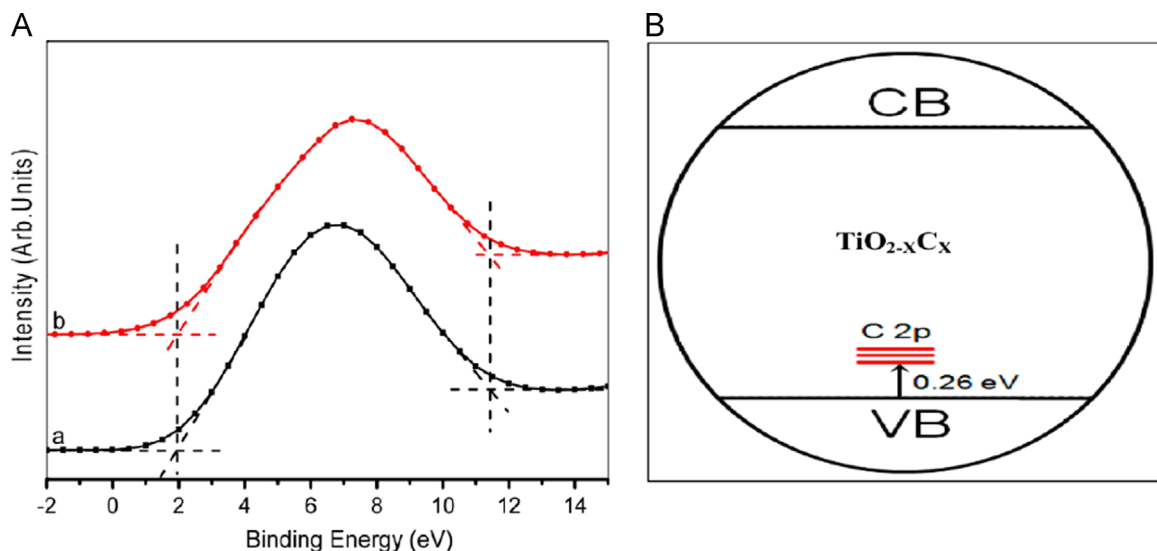

Fig. 3. (A) VB XPS spectra of (a) anatase and (b) carbon-doped anatase-brookite hetero-junctions prepared (B) Localised impurity levels for C-doped TiO_2. (Etacheri, Michlits, Seery, Hinder and Pillai, ACS Appl. Mater. Interfaces 5 (2013) 1663. Copyright 2010, reprinted with permission from American Chemical Society.
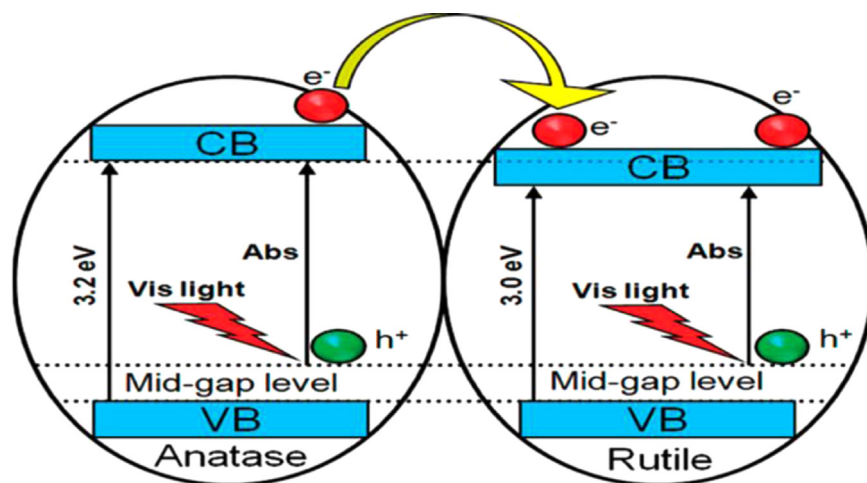
Fig. 4. : Schematic diagram showing electron transfer in anatase–rutile heterojunctions in visible light photocatalysts. (Etacheri, Seery, Hinder and Pillai, Inorg. Chem. 51 (2012) 7164.) Copyright 2012, reprinted with permission from American Chemical Society.

above [48,55,63-65,70]. It was noted that the combined effect of superior electron–hole separation and substitutional doping by nitrogen promoting band gap narrowing was found to have an enhancing effect on the photocatalytic behaviour of the heterojunction [63]. When analysing a co-doped system of S,N–TiO$_2$ anatase–rutile heterojunction [63], it was the formation of S 3p, N 2p and π∗ N–O states between the conduction band and the valence band that was responsible for its band gap narrowing. The efficient electron–hole separation within this system was ascribed as the most important factor for the superior visible light induced photocatalytic activity of the heterojunction.

The use of these solar and visible light active photocatalysts in the treatment of contaminants of emerging concern (CECs), endocrine disrupting compounds (EDCs), bacteria and cyanotoxins are to be discussed in detail in this review.

3. Visible light active TiO$_2$ photocatalysts for treating contaminants of emerging concern (CEC)

The acknowledgement of the ever increasing issue of contaminants of emerging concern (CECs) has increased in recent years. CECs come from a broad spectrum of sources such as but not limited to pharmaceuticals [90], steroids [91], antibiotics [92–94], phthalates [95], disinfectants [96], pesticides [97], fragrances (musk) [98,99], preservatives and additives [100]. From definition, the issue with CECs is that they are synthetic or naturally occurring chemicals but are not commonly monitored in the environment. These have the potential or are suspected to cause adverse ecological and/or human health effects. CECs may be either chemicals that have been around for a long time but have not been suspected of having negative environmental effects, or new emerging products of which their properties, effects, and environmental implications may not be fully known. One main concern with the identification of these CECs in the environment is that it is clear that existing wastewater treatment processes are ineffective in their removal [101,102]. Removal of CECs using conventional treatment methods (e.g. physical, chemical or biological) is inefficient and the operation cost is significantly high. Additionally, a number of EU directives such as 85/337/EEC, 91/271/EEC, 76/464/EEC, 2010/75/EU and 2006/118/EC limit the use of conventional technologies due to their ineffectiveness and incomplete bio-degradation of the waste products. Here we will discuss the use of TiO$_2$ as a material of interest in the degradation of these contaminants.

Several publications have highlighted the use of TiO$_2$ in the removal of contaminants from wastewater systems [103–112]. Miranda-Garcia et al. studied the use of immobilized TiO$_2$ in the destruction of fifteen selected emerging contaminants in simulated and real effluent wastewater using solar irradiation (Fig. 5) [113]. Typically, TiO$_2$ is used in a suspension (slurry) form making its removal from the treated water difficult. To avoid this complication, immobilized TiO$_2$ on a borosilicate glass support was utilized. The immobilized TiO$_2$ was seen to not only degrade most of the 15 contaminants, but also showed great reusability even after 5 reuses in the simulated water system. Using real effluent water, the pollutant degradation time using immobilised TiO$_2$ was shorter or equal to that using TiO$_2$ in suspension.

One pollutant in particular, carbamazepine (CBZ), proved to be a persistent compound, rarely or not at all degraded in wastewater treatment plants. Carbamazepine is a derivative of dibenzazepine, structurally similar to tricyclic antidepressants, used primarily in the treatment of epilepsy, relief of neuralgia and psychotic disorders. With CBZ deemed to be a danger to aquatic life including bacteria, algae, invertebrates and fish, and with its presence detected in influent, effluent and sludge samples from wastewater treatment plants (WWTPS) [114], methods to increase the removal of this pollutant are required. Using solar irradiation, Haroune et al. were able to show effective degradation of CBZ and three of its metabolites; carbamazepine epoxide (CBZ-E), acridine (AI) and acridone (AO), using TiO$_2$ photocatalysis. They further suggested that the impact of factors such as pH, ionic strength and natural organic matter play a role in either enhancing or inhibiting this removal [115]. Efforts to shift the band gap of TiO$_2$ to the visible region were also explored to enhance the CBZ degradation under solar conditions. By coating a thin film of N-doped TiO$_2$ onto a glass slide, Mamane et al. hoped to shift the light absorption edge from UV to visible light in order activate the photocatalytic degradation of chemical and biological pollutants using solar light [116]. It was revealed that even though a shift toward absorbance of longer wavelengths of light occurred, the shift was not large enough to allow the absorption of visible light resulting in low reactivity over 400 nm. Hydroxylated reaction intermediates of CBZ showed attacks on the aromatic ring by hydroxyl radicals. Tri-doping TiO$_2$ with dopants such as C, N and S to produce visible light active TiO$_2$ was explored by Wang et al. [117]. Using this method, a successful band gap reduction occurred producing a material with a band gap of 2.67 eV. Using a visible-LED photoreactor utilizing a 450 nm light source, a 68% CBZ removal was seen over 120 min. As the water supply is only present in WWTPS
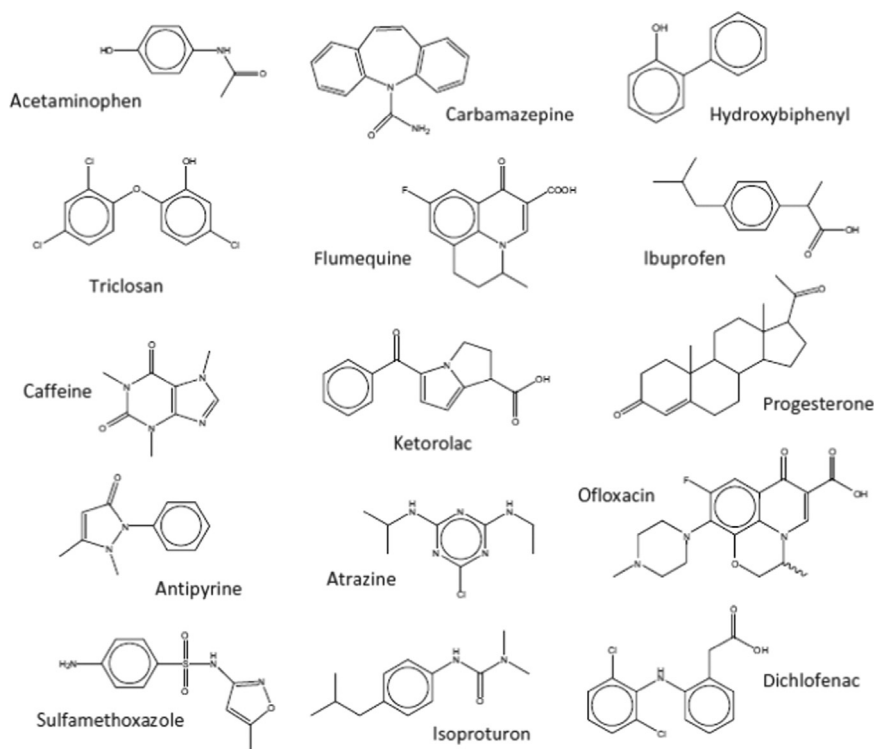
Fig. 5. Structure of selected emerging contaminants. (Miranda-García et al. Applied Catalysis B: Environmental 103 (2011) 294–301). Copyright 2015, reprinted with permission from Elsevier.

for a relatively short amount of time, quick removal of these pollutants is preferred.

4. Photocatalytic treatment of endocrine disrupting compounds (EDCs)

Endocrine disrupting compounds (EDCs) are chemicals that have xenobiotic or exogenous origins that can interfere and alter the function of the endocrine system and consequently cause adverse health effects in animals and humans [118–125]. Several substances have already been classified as or as having the potential to be EDCs (Fig. 6), including compounds from the groups of polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), organotins (OTs), volatile organic compounds (VOCs), pesticides, and heavy metals [126–133].

Other substances of interest are natural and synthetic estrogenic and androgenic chemicals [134,135]. These chemicals have found to exist in wastewater, surface water, sediments,

Fig. 6. Chemical structures of selected EDCs.

groundwater, and even drinking water and have been attributed to disturbances in the reproductive systems of humans and wildlife [136]. Since conventional wastewater treatment methods have been proven to be ineffective at removing or degrading these chemicals, various other avenues of research must be investigated as potential removal routes [137–140]. The use of TiO_2 under visible light and solar light irradiation is reported here.

Bisphenol A (BPA) is a synthetic compound known to be an EDC. With uses primarily in the production of plastics including the lining of food and beverage packaging and baby bottles, and the potential for BPA to impose estrogenic and toxicological risks, significant attention has been made in recent years to remove this threat [141–146]. Using nitrogen doped TiO_2 hollow spheres, Subagio et al. was able to produce a 90% removal of BPA using vis-LED conditions (465 nm) when compared to TiO_2 and hollow spheres individually [147]. It was reported that the incorporation of the hollow spheres into the N–TiO_2 system led to the development of an enhanced surface area and an increased porosity which in turn allowed for the development of an increased photonic efficiency. Alkaline conditions were deemed to be favourable during the analysis with the production of hydroxyl radicals being attributed to the improved degradation results. Wang et al. reported the use of a co-doping system, CN–TiO_2, against BPA using visible light irradiation [148]. In this report, the group suggested that it is the synergistic properties that appear when combining C and N that were responsible for the increased photocatalytic ability of the prepared materials. The mesoporous system with a high surface area provided favourable conditions for the diffusion and adsorption of the BPA molecules. A 96% removal of BPA after a two hour period, with complete elimination after five hours, was seen. It was surmised that when using white light, as opposed to other blue, green and yellow LEDs a higher amount of valence band electrons were excited to the conduction band, leading to an improved photocatalytic degradation rate. The results of the study by Wang et al. are in agreement with those of Subagio et al. in that
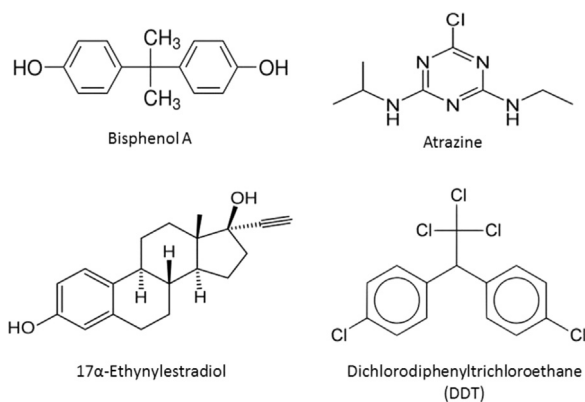
an increase in pH led to the greater number of hydroxyl radicals available. It was also noted that when the pH was increased to an alkaline state, a repulsion of the BPA molecules from the CN–TiO$_2$ surface was detected, leading to the conclusion that a more circumneutral pH, $5 < pH < 9$, was optimum for BPA degradation. Composite systems of nitrogen doped TiO$_2$ supported on activated carbon (AC) under solar irradiation [149] and Cu–TiO$_2$ under visible light irradiation [150] have also been studied as potential technologies for BPA removal from aqueous systems.

Hormone steroids are naturally present in the environment due to their excretion by animals and humans [151,152] and efforts have been made to detect and identify their presence in wastewater sources [153]. Natural estrogenic steroids are secreted from the ovary and placenta by humans and animals and examples of such are estrone (E1) and 17β-estradiol (E2). 17-α-ethynylestradiol, a commonly used synthetic estrogenic steroid, is excreted into the environment through the use of oral contraceptive pills and is known to be responsible for altering the reproduction of fish and effecting the sustainability of some fish species [154–157]. Numerous studies into the removal of this steroid from various water sources have been conducted [158], including the use of UV irradiation [159–161] and more recently, solar irradiation with the photocatalyst TiO$_2$ [135,139,161–163]. Oliveira et al. [135] studied the use of a TiO$_2$/WO$_3$ system, deposited on electrodes, for the remediation of EE2 from aqueous solutions using solar irradiation. Three systems were analysed; heterogeneous photocatalysis (HP), electrochemically-assisted heterogeneous photocatalysis (EHP) and photolysis, with the EHP system proving to be the most efficient system. Upon the addition of a photo-anode (Pt wire) into the solution, set at 0.7 eV, EE2 removal was seen to increase possibly due to the suppression of the electron–hole recombination under these conditions. The results concluded that the addition of the WO$_3$–TiO$_2$ improved the sunlight harvesting capabilities of the system and enhanced the photo-induced charge separation due to the relative positions of the TiO$_2$ and WO$_3$ conduction bands and valence bands.

DDT (dichlorodiphenyltrichloroethane) is an organochlorine insecticide primarily used between the 1940s to the 1970s with initial uses in the treatment of malaria, typhus, and the other insect-borne human diseases. After concerns arose about its effect on both wildlife and human health, and its tendency to bioaccumulate in the food chain, prohibitions and restrictions began for the use of this compound. After being banned in 1972, over 100 countries signed the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001, committing to the elimination of 12 POPs including DDT, with an increase to 160 committed countries by 2008. Other than the allowance of the World Health Organisation (WHO) who permitted the use of DDT for indoor removal of malaria, DDT is only permitted for use when no other safe, effective or affordable methods are available [164]. DDT is seen to directly affect the liver, the central and the peripheral nervous systems [165]. The removal of this compound and its derivatives has been studied in recent years using both UV [165,166] and visible light photocatalysis [167] in aqueous solutions. Using an N-doped TiO$_2$ prepared using diethandamine (DEA) as the dopant source, Ananpattarachai et al. [167] showed the degradation of DDT under both UV and visible light irradiation. Analysing both methods, visible light showed a 6 times higher rate of removal than use of UV light, with 100% of DDT removed. This highlighted the use of photocatalysis in the remediation of DDT in environmental water supplies with further promise of its use in real contaminated water systems.

Atrazine (ATR), a regularly used herbicide, is frequently found in the effluent of wastewater treatment plants [102,168] and is a common soil and water pollutant. ATR is an EDC of importance due to its potential to have disruptive impacts on the reproductive gland formation of amphibians. As with other pollutants,
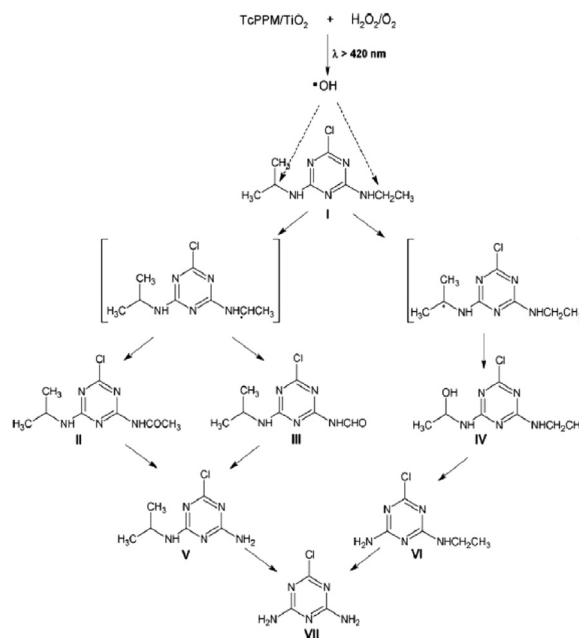

Fig. 7. Reaction by-products of atrazine degradation using visible light irradiation. (Granados-Oliveros et al., Appl. Catal. B Environ. 89 (2009) 448). Reprinted with permission from Elsevier.

conventional methods of water treatment are impractical as only partial elimination of ATR can be seen. The use of metalloporphyrins supported on TiO$_2$ as a potential system for ATR removal utilising visible light has been studied. Granados-Oliveros et al. [169] prepared, analysed and compared metalloporphyrin systems with four different metal centres; Cu(II), Fe(III), Zn(II) and metal-free, for their photocatalytic degradation activities. It was deemed that a system of copper(II) tetra (4-carboxyphenol) porphyrin (TcPPCu(II)) was the best photocatalyst with 82% reduction in ATR after a one hour period (Fig. 8). Study of the ROS production from this system indicated that O$_2^{\bullet-}$ alone was not responsible for the reactivity, yet upon the addition of H$_2$O$_2$ into the reaction solution, increased reactivity was seen. It was deduced that the H$_2$O$_2$ was reduced by O$_2^{\bullet-}$ and/or e$_{cb}$ to the $^{\bullet}$OH species which in turn increased reactivity. It was surmised that the $^{\bullet}$OH attacked the amino alkyl groups freeing organic radicals generated from a very quick hydrogen atom abstraction from the substrate. Intermediates II, III and IV were produced from a subsequent alkylic oxidation reaction followed by a dealkylation to produce the V, VI and VII intermediate products (Fig. 7). This report suggests that as no photoproducts were observed from the dehalogenation of ATR by electron transfer, it can be said that the $^{\bullet}$OH are responsible for the ATR oxidation process. NF doped TiO$_2$ systems have also been analysed for ATR elimination under visible and solar irradiation [170,171].

5. Photocatalytic anti-bacterial action

The use of semiconductors as effective anti-bacterial materials has been greatly documented in the past [29,172–175]. Here we discuss recent publications in the field which utilise visible light responsive titanium dioxide in order to make it a viable route for applications in industries such as environmental, hospital and wastewater treatment. Several different doping systems including nitrogen [176], nitrogen–silver [72,177], nitrogen–copper [47], sulphur [178], carbon [64], nickel [179], copper [179] and more recently graphene nano-sheet [180] doped TiO$_2$ (the term doping is loosely used here for addition, decoration, doping, incorporation
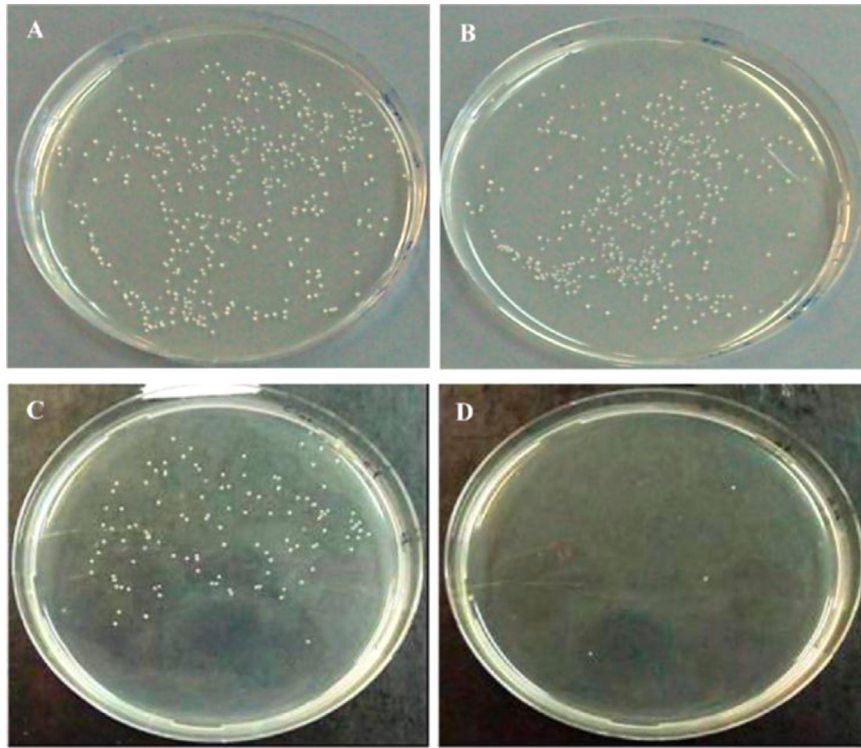
Fig. 8. Example of anti-bacterial action by titania photocatalysts. (A) Evonik-Degussa P-25 with no light. (B) C-doped anatase-brookite heterojunctions with no light. (C) Evonik-Degussa P-25 catalyst with visible light irradiation. (D) C-doped anatase-brookite hetero-junctions with visible-light irradiation. Reproduced from Etacheri, Michlits, Seery, Hinder and Pillai, Appl. Mater. Interfaces 5 (2013) 1663–1672; Reprinted with permission from American Chemical Society.

etc.) have been prepared and analysed for their inactivation of various bacteria strains such as *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Salmonella typhimurium,* and *Micrococcus lylae.* It is widely reported that the photocatalytic killing mechanism of bacteria starts with damaging the cell membrane resulting in the subsequent leakage of internal bacterial components from the damaged sites. Subsequently, the leaked cell debris is oxidised by photocatalytic reactions. Pulgarin's group have reported in great detail the effects nitrogen and sulphur doping of TiO$_2$ and its killing of *E. Coli* as the bacteria of choice [181–184]. In their earlier work, they suggested that a co-doped TiO$_2$ using thiourea as a source of N and S was a viable system for *E. Coli* destruction [181]. Upon thermal treatment of the materials, 400 or 500 °C, they were able to determine that the differing thermal temperatures produced differing doping species. The authors were able to conclude from their study that it is the nature of the doping (substitutional or interstitial N-doping and cationic or anionic S-doping), surface hydroxylation, and the particle size that plays a role in the ROS formation. With continuous study of this system, the group suggested that under visible light irradiation, it is the formation of the superoxide anion radical O$_2$$^{\bullet-}$ and the singlet oxygen (^{1}O$_2$), produced by photo-promoted electron from the N and S localised states, which are responsible for *E. Coli* inactivation [182,183]. Solar irradiation was also studied by Pulgarin's group for its ROS generation [184]. It was determined that under UV light, the inactivation of *E. Coli* was due to preferred hydroxyl radical ($^{\bullet}$OH) formation through water oxidation by photo-induced valence band holes. Etacheri et al. [64] reported that a carbon doped TiO$_2$ anatase–brookite heterojunction in the ratio of 80/20 provided sufficient inactivation of *S. aureus* under visible light irradiation. Significant band gap narrowing was caused by the formation of additional energy levels by carbonate ions which in turn resulted in superior photocatalytic and antibacterial activities. Examples of the anti-bacterial action of the material are seen in

Fig. 8. It is the slower rate of electron-hole recombination that explains the increased activity of the C–TiO$_2$. When studying the roles of the ROS, the H$_2$O$_2$ produced from the reaction of surface absorbed H$_2$O or OH$^-$ reacts with $^{\bullet}$OH to form the protonated superoxide radical $^{\bullet}$HO$_2$ that functions like O$_2$$^{\bullet-}$ to inactivate bacterial cells. The proposed mechanism of anti-bacterial action is given in Fig. 9. Here it is shown that upon activation with light, an electron is promoted from the valence band to the conduction band providing a positive hole in the valence band and an electron in the conduction band. The generated ROS such as O$_2$$^{\bullet-}$, ^{1}O$_2$, $^{\bullet}$OH, H$_2$O$_2$ and $^{\bullet}$HO$_2$ result in the decomposition of bacteria. From these studies it can be concluded that it is not only the material of interest that needs to be considered but also the types and concentrations of ROS being generated under solar/visible light conditions.

6. Photocatalytic treatments of cyanotoxins

Cyanobacteria or blue–green algae (blooms) are photosynthetic bacteria that share some properties with algae and are naturally present in lakes, streams, ponds, and other nutrient rich surface waters. By consuming oxygen in the environment, they create a hypoxic condition which causes die-off in plants and animals. There are several factors that influence the growth of these blooms. These include light intensity, total sunlight duration, nutrient availability such as nitrogen and phosphorous, water temperature, pH and water flow [185]. Under favourable conditions of light and nutrients, some species of cyanobacteria produce toxic secondary metabolites, known as cyanotoxins. These have many harmful effects in relation to human [186,187], animal [188] and environmental health. Microcystins are stable, water-soluble molecules and are rapidly absorbed by the liver resulting in harmful results such as cell necrosis, haemorrhage and death [189].
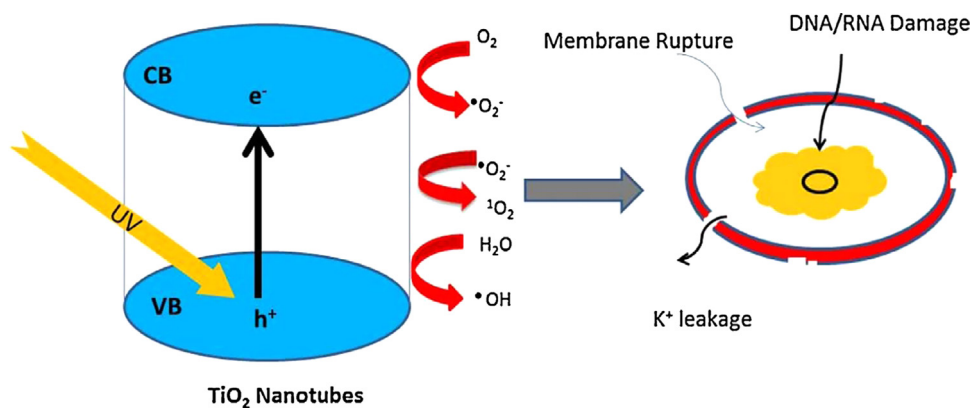
Fig. 9. Proposed mechanism of anti-bacterial action by photocatalysis. (Podporska-Carroll et al. Appl. Catal. B Environ. 176–177 (2015) 70). Copyright 2015, reprinted with permission from Elsevier.

In recent years, significant attention has been given to the ever rising problem of these cyanotoxins occurring in aquatic sources, especially those that serve as sources of drinking water supply [189–201]. Choi et al. [202] in 2007 reported that when using a visible light active (VLA) N–TiO$_2$ material under acidic conditions (pH 3.5), the adsorption and photocatalytic degradation of MC-LR is greatly improved. It was proposed that electrostatic attraction forces between MC-LR and N–TiO$_2$ are increased when MC-LR has an overall negative charge due to the dissociation of its free carboxylic groups and N–TiO$_2$ is positively charged under these conditions. Due to the very short lifetime of the hydroxyl radicals and that the reaction mainly occurs with adsorbed species, the improved surface adsorption of MC-LR to the TiO$_2$ surface is central to MC-LR degradation. It has been determined that MC-LR degradation occurs at four sites of the structure; the aromatic ring, the methoxy group, conjugated double bond of the Adda group and the cyclic structure of the Mdha amino acid. Antoniou et al. [203] studied the use of immobilised TiO$_2$ as a photocatalyst for MC-LR and reported that the preferred site of hydroxyl radical attack for MC-LR is the conjugated double bonds of the Adda moiety, which is also suggested in the work of Anderson et al. based on the use of visible light irradiation in the degradation of the MC-LR compound [204] (Fig. 10). Antoniou et al. discusses two different mechanistic steps which occur upon the reaction of •OH with the diene bonds producing hydroxyl adducts; hydroxyl addition and hydroxyl substitution [205] (Fig. 11). Initial incorporation of the •OH into the double bond results in the formation of an allyl radical, with subsequent •OH reacting with the carbon centre. The double hydroxylation occurs at any of the double bond pairs available. A mixture of products may form upon electrophilic reactions of the conjugated dienes, caused by the various resonance configurations that the allyl radical can take. The product formed depends on the stability of the allyl radical. Isomerisation at the C$_4$–C$_5$ or C$_6$–C$_7$ of the diene bond of the Adda chain is due to the •OH addition mechanism and not the effect of light irradiation. Hydroxyl substitution is responsible for the OH substitution for hydrogen of C$_7$ forming enol–MC-LR. This product rapidly undertakes several reactions including isomerization to a more stable tautomer of ketone–MC-LR. This further undergoes a series of oxidative induced bond cleavage mechanistic steps resulting in a hydroxyl derivative. During the study of the degradation pathway of MC-LR, the group concluded that the main •OH mechanistic steps were hydroxylation through addition or substitution with simultaneous isomerization, oxidation and oxidative bond cleavage [205].

The synthesis of a visible light active NF–TiO$_2$ material with a reduced effective band gap of 2.85 eV (435 nm) with the addition of a fluorosurfactant and with improved physiochemical properties such as surface area, crystal size and porosity has been reported [206]. It was suggested that an anatase/brookite
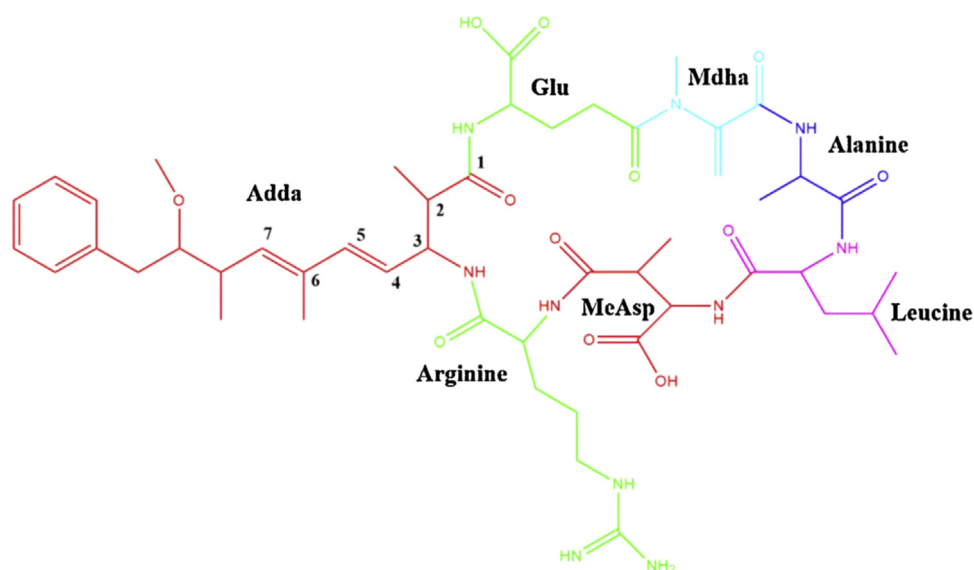

Fig. 10. Structure of microcystin-LR. (J. Andersen et al. Applied Catalysis B: Environmental 154–155 (2014) 259–266). Reprinted with permission from Elsevier.
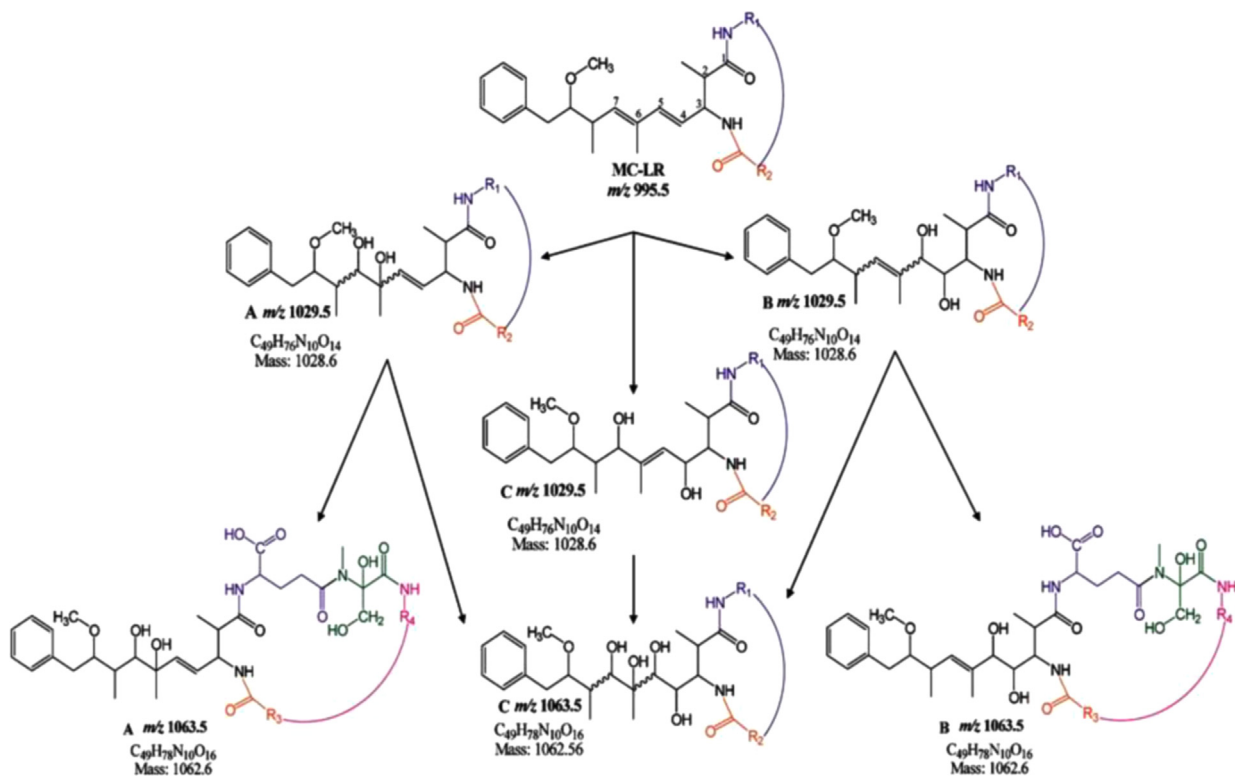
Fig. 11. Attack of hydroxyl radicals on the conjugated carbon double bonds of Adda. Reproduced from Environ. Sci. Technol. 42 (2008) 8877–8883; with permission from American Chemical Society.

heterojunction was partly responsible for the increased photocatalytic efficiency due to the quick interparticle electron transfer between the constituent titania nanocrystals that slows down recombination losses. The brookite surface allows for improved water adsorption and consequently increases the photo induced hydrophilic conversion and surface reactivity through the formation of abundant $\bullet$OH integral for pollutant adsorption on the photocatalyst surface. Further research into the utilization of visible light active NF–TiO$_2$ as a model material for the destruction of MC-LR has been carried out in further detail by Pelaez et al. [206–208]. In several published papers by this group, details on the role of water quality parameters, material doping and the formation of ROS have been discussed. Under favourable acidic conditions, it was found that by sparging a solution of pollutant and photocatalyst with oxygen, an increase in the presence of hydroxyl radicals and singlet oxygen can be detected [207]. This is due to the production of superoxide anion radicals through the scavenging effect of conduction band electrons by the dissolved O$_2$ molecules. Upon the reduction of oxygen, the rate of ROS production is decreased due to the increased rate of recombination taking place. Incorporation of different additives to improve and/ or control the physiochemical properties of the photocatalyst was also studied. The addition of Evonik/Degussa P25 into visible light active NF–TiO$_2$ was found to play a significant role in improving BET surface area, pore volume, porosity and the total TiO$_2$ mass content in the film [208]. Triantis et al. [209] reported the mineralisation of MC-LR under various light sources. When irradiated with visible light over a wavelength of >410 nm, standards such as Evonik/Degussa P25 and TiO$_2$ were seen to be completely inactive whereas the degradation of the toxin was easily achieved by N–TiO$_2$ due to a red-shift of the energy band gap to the visible light region (2.3 eV). Liu et al. [210] also studied the activity of visible light active co-doped TiO$_2$ (C–N TiO$_2$) with the effective narrowing of the band gap by carbon and nitrogen. Favourable structural and textural characteristics such as small crystalline

size, anatase formation, increased porosity and a high specific surface area with successful inhibition of the anatase to rutile phase transformation were considered the reasons for the increased photocatalytic activity of these materials for MC-LR degradation. Zhao et al. [211] showed that a visible light active NF–TiO$_2$ proved to be effective in the destruction of 6-hydroxymethyl uracil (6-HOMO), a model compound (Fig. 12) for the cyanotoxin Cylindrospermopsin (CYN).

This study also compared the effectiveness of the different doping systems including PF–TiO$_2$ and S–TiO$_2$. It was seen that of the three systems, PF–TiO$_2$ had the largest shift towards the visible light region (2.68 eV), yet it was less effective than NF–TiO$_2$ (2.75 eV). The suggested reason for this was that doping with PF resulted in poorer structural properties and a faster electron–hole recombination rate. The slower recombination rate of the NF–TiO$_2$ system allowed for the production of ROS products which in turn promoted the destruction of this compound. The active species found in this study was the superoxide radical anion (O$_2^{\bullet-}$) at the conduction band which as discussed before, can result in the generation of hydroxyl radicals through the reaction of oxygen with H$_2$O$_2$ (Fig. 13). This indicated that molecular oxygen is required for degradation as an e_{cb}^- trap and/or in the production of O$_2^{\bullet-}$. S$-$TiO$_2$ was proven to be an inactive system for this reaction. This study furthered the knowledge and the roles of ROS in doped and co-doped titanium dioxide photocatalysts.

Graphene oxide (GO) is a material of particular interest for the doping of TiO$_2$ due to its abundant anchoring sites for binding with the photocatalysts. Fotiou et al. [212] attempted to use GO to increase the photo-activity of TiO$_2$ against MC-LR under UV-A and solar irradiation (Fig. 14). From the characterisation of the GO doped materials, it can be clearly seen that the resulting material absorbs light from the whole visible region. After a period of 1 h irradiation using solar irradiation, Degussa P25 was seen to fully degrade MC-LR with GO–TiO$_2$ closely behind with 97% followed by another standard Kronos (95%) and reference TiO$_2$ (18%). The
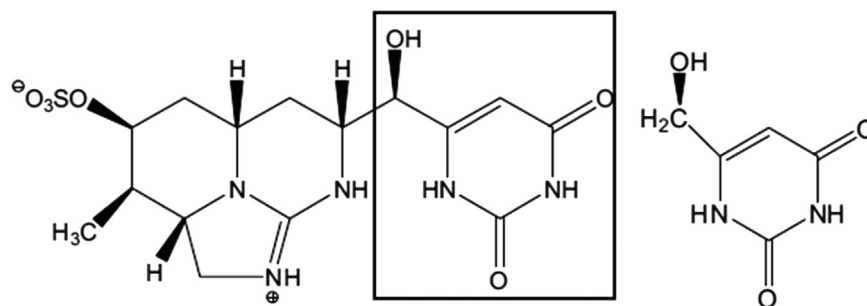
Fig. 12. Chemical representation of cylindrospermopsin (CYN) and the model compound 6-hydroxymethyl uracil (6-HOMU). Adapted from Zhao et al., Catal. Today 224 (2014) 70; Copyright 2014, reprinted with permission from Elsevier.
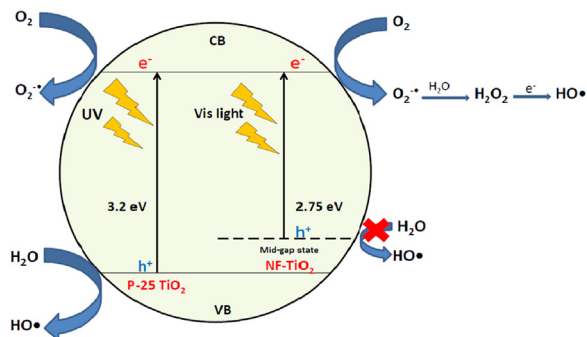

Fig. 13. Visible light photocatalytic processes for the destruction of 6-hydroxymethyl uracil. Adapted from Zhao et al., Catal. Today 224 (2014) 70; Copyright 2014, reprinted with permission from Elsevier.

improved activity of GO–TiO$_2$ compared to the reference TiO$_2$ was attributed to the effective inhibition of the electron–hole recombination route due to the interfacial charge transfer process. The doping with GO provided carbon for the substitution of oxygen (Ti–O–C) which in turn provided new energy states deep in the TiO$_2$ band gap resulting in visible light absorption. Intermediate products produced by GO–TiO$_2$ degradation of MC-LR were identified using LC-MS. These intermediates were determined to be mostly identical to those identified by P25 under UV-A suggesting that the photo-generation mechanism takes place through a common active species, •OH. The reaction me-

chanism suggested was in accordance with that provided by Antoniou previously confirming that the responsible reaction steps are hydroxyl addition and hydroxyl substitution [205]. Further studies where the materials were tested against MC-LR in surface water supplies have shown that GO–TiO$_2$ is almost as effective as in ultra-pure water, highlighting the promising use of this material in water treatment systems.

7. Conclusions

Research into the development of solar and visible light active photocatalysts for the treatment of contaminants of emerging concern (CECs), endocrine disrupting compounds (EDCs), bacteria and cyanotoxins has been discussed in detail throughout this report. The use of conventional water treatment technologies against these contaminants are limited due to their ineffectiveness and incomplete bio-degradation of the waste products as outlined in a number of EU directives such as 85/337/EEC, 91/271/EEC, 76/464/EEC, 2010/75/EU and 2006/118/EC. Therefore, the effective utilisation of solar and visible light for the destruction of these pollutants has great potential. As discussed, upon activation with light of a suitable wavelength, reactive oxygen species (ROS) such as O$_2$•$^-$, ^{1}O$_2$, •OH, H$_2$O$_2$ and •HO$_2$ are produced with the ability to degrade organic compounds. It was found that it is not only the material of interest that needs to be considered but the production of ROS being generated under solar/visible light conditions is also vital. It can be concluded that there is a critical need for further improvement of the efficiency of these materials for bulk industrial use.
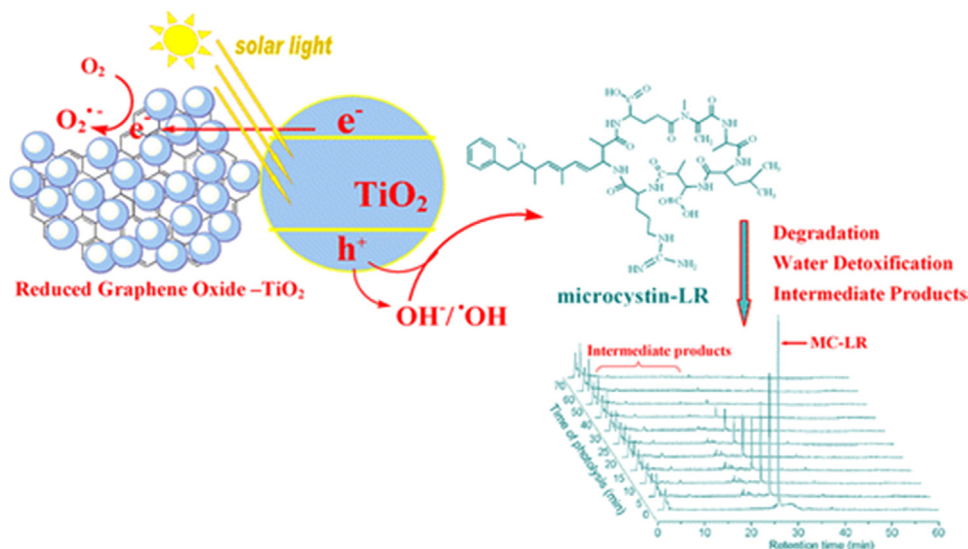

Fig. 14. Proposed mechanism for the degradation of MC-LR using RGO–TiO$_2$ under solar irradiation. Reproduced from Ind. Eng. Chem. Res. 52 (2013) 13991–14000; Reprinted with permission from American Chemical Society.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.mssp.2015.07.052.

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