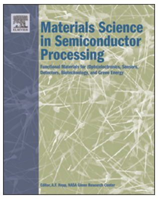
Materials Science in Semiconductor Processing ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/matsci



A review of solar and visible light active TiO_2 photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern

Rachel Fagan [a,b], Declan E. McCormack [a,b], Dionysios D. Dionysiou [c], Suresh C. Pillai [d,e,*]

[a] Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland
[b] School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland
[c] Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), 705 Engineering Research Center, University of Cincinnati, Cincinnati, OH 45221-0012, United States
[d] Nanotechnology Research Group, Department of Environmental Science, Institute of Technology Sligo, Sligo, Ireland
[e] Centre for Precision Engineering, Materials and Manufacturing Research (PEM), Institute of Technology Sligo, Sligo, Ireland

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form
16 July 2015
Accepted 20 July 2015

Keywords:
Photocatalytic
Graphene
Disinfection
Emerging contaminants
Antibiotics
Steroids

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.

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 photoexcited electron is promoted from the filled valence band (VB) of semiconductor photocatalyst to the empty conduction band (CB)

---

* Corresponding author.
E-mail address: Pillai.suresh@itsligo.ie (S.C. Pillai).

http://dx.doi.org/10.1016/j.mssp.2015.07.052
1369-8001/© 2015 Elsevier Ltd. All rights reserved.

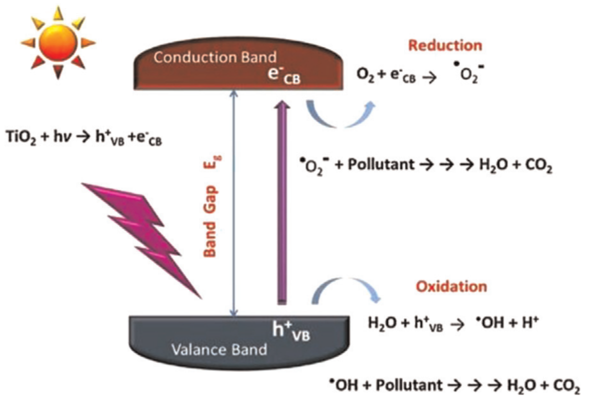


Fig. 1. Schematic illustration of the photocatalytic process. (Banerjee, Dionysiou and Pillai, Appl. Catal. B Environ. 176–177 (2015) 396). Copyright 2015, reprinted with permission from Elsevier.

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 ($\geq$ 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 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

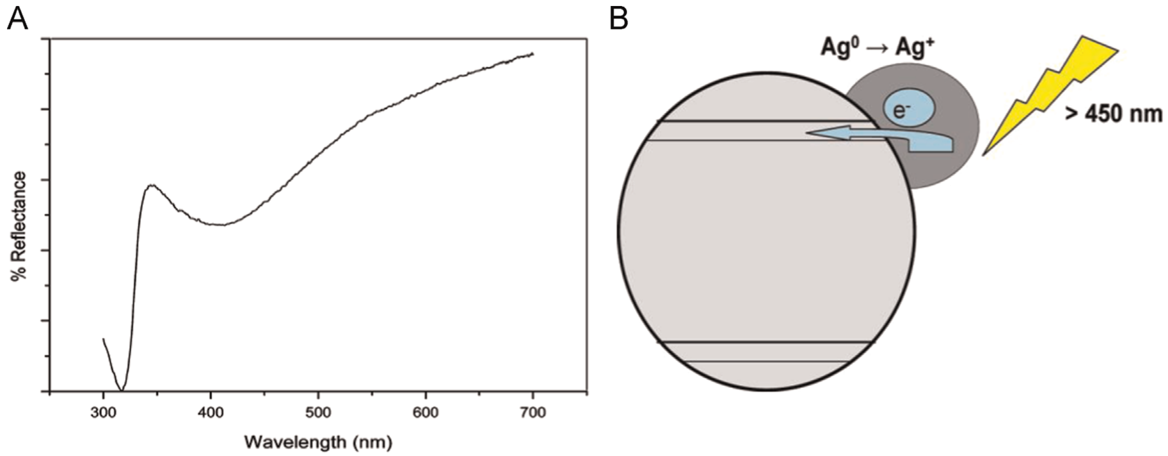


Fig. 2. (A) Diffuse reflectance spectrum of silver nanoparticles b) Schematic diagram showing the mechanism for light absorption of Ag nanoparticles. (Nolan , Seery, Hinder, Healy and Pillai, J. Phys. Chem. C 114 (2010) 13026) reprinted with permission from American Chemical Society.

Please cite this article as: R. Fagan, et al., Materials Science in Semiconductor Processing (2015), http://dx.doi.org/10.1016/j.mssp.2015.07.052