Journal of Photochemistry and Photobiology C: Photochemistry Reviews 25 (2015) 1–29

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology C: Photochemistry Reviews

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

Review

Visible-light activation of TiO_2 photocatalysts: Advances in theory and experiments

Vinodkumar Etacheri[a,b], Cristiana Di Valentin[c], Jenny Schneider[d], Detlef Bahnemann[d,e], Suresh C. Pillai[f,g,*]

[a] School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, United States
[b] Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland
[c] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 55, 20125 Milano, Italy
[d] Institut fuer Technische Chemie, Gottfried Wilhelm Leibniz Universitaet Hannover, Callinstrasse 3, D-30167 Hannover, Germany
[e] Laboratory for Nanocomposite Materials, Department of Photonics, Faculty of Physics, Saint-Petersburg State University, Ulianovskaia str. 3, Peterhof, Saint-Petersburg 198504, Russia
[f] Nanotechnology Research Group, Department of Environmental Science, Institute of Technology Sligo, Sligo, Ireland
[g] Centre for Precision Engineering, Materials and Manufacturing Research (PEM), Institute of Technology, Sligo, Sligo, Ireland

ARTICLE INFO

Article history:
Received 25 April 2015
Received in revised form 17 August 2015
Accepted 24 August 2015
Available online 28 August 2015

Keywords:
Photo-induced reactions
Solar energy
Mechanism
Fundamentals
Doping
Graphene
Energy and environmental
Air pollution
Sustainable
Photovoltaic
Hydrogen production
Tutorial review

ABSTRACT

The remarkable achievement by Fujishima and Honda (1972) in the photo-electrochemical water splitting results in the extensive use of TiO_2 nanomaterials for environmental purification and energy storage/conversion applications. Though there are many advantages for the TiO_2 compared to other semiconductor photocatalysts, its band gap of 3.2 eV restrains application to the UV-region of the electromagnetic spectrum ($\lambda \leq 387.5$ nm). As a result, development of visible-light active titanium dioxide is one of the key challenges in the field of semiconductor photocatalysis. In this review, advances in the strategies for the visible light activation, origin of visible-light activity, and electronic structure of various visible-light active TiO_2 photocatalysts are discussed in detail. It has also been shown that if appropriate models are used, the theoretical insights can successfully be employed to develop novel catalysts to enhance the photocatalytic performance in the visible region. Recent developments in theory and experiments in visible-light induced water splitting, degradation of environmental pollutants, water and air purification and antibacterial applications are also reviewed. Various strategies to identify appropriate dopants for improved visible-light absorption and electron–hole separation to enhance the photocatalytic activity are discussed in detail, and a number of recommendations are also presented.

Contents

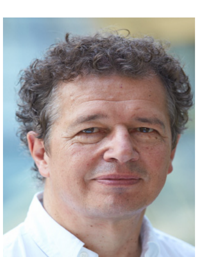
* Corresponding author at: Nanotechnology Research Group, Department of Environmental Science, Institute of Technology Sligo, Sligo, Ireland.
E-mail address: pillai.suresh@itsligo.ie (S.C. Pillai).

http://dx.doi.org/10.1016/j.jphotochemrev.2015.08.003

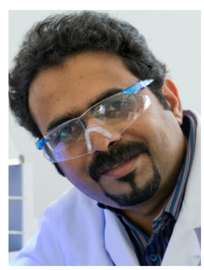
Dr. Vinodkumar Etacheri obtained his PhD in Materials Chemistry from Dublin Institute of Technology (DIT), Ireland in 2011. This work under the guidance of Prof. Suresh C. Pillai involved the development of new generation visible-light active TiO_2 nanomaterials. He then completed postdoctoral research at Bar Ilan University, Israel, and University of Michigan, USA in the area of Li-ion and Li-O_2 batteries. Currently he is working as a research associate at Purdue University, USA, developing nanomaterials for a wide range of electrochemical energy storage systems. His research areas extent from semiconductor photocatalysis for environmental remediation, antibacterial applications, and water oxidation, to engineering of carbon and metal oxide based electrodes for rechargeable batteries and supercapacitors.

Prof. Cristiana Di Valentin was born in Maniago (PN), Italy on 29/07/1973. She graduated in Chemistry in 1997 at the University of Pavia where she also received her Ph.D. degree in 2000 in collaboration with the Technische Universität München. She was appointed by the University of Milano-Bicocca as Assistant Professor in 2002 and as Associate Professor in 2012. She has been visiting scientist at the Technische Universität München, Universitat de Barcelona, Ecole Nationale Superieure de Paris and Princeton University. Her research activity spans from *ab initio* computational study of reaction mechanisms in organic chemistry and homogeneous catalysis to heterogeneous catalysis, photocatalysis, doped and defective semiconducting oxides, graphene and carbon based materials for fuel cells.

Jenny Schneider received her M.Sc. degree in Material- and Nanochemistry in 2011 from the Gottfried Wilhelm Leibniz University Hannover. She is currently a Ph.D. student with Prof. Bahnemann at the Gottfried Wilhelm Leibniz University Hannover, investigating the reaction dynamics of photogenerated charge carriers in different photocatalysts by means of laser flash photolysis spectroscopy. Her research interests include the mechanism(s) of photocatalysis, the detailed understanding of photocatalytically induced chemical conversions as well as theoretical simulations of photocatalytic processes.



Prof. Dr. rer. nat. habil. Detlef Bahnemann has received his PhD in Chemistry from the Technical University Berlin in 1981 and his Habilitation in the area of Technical Chemistry from the Leibniz University Hannover in 2012. He is currently the Head of the Research Unit "Photocatalysis and Nanotechnology" at the Institute of Technical Chemistry of the Leibniz University Hannover in Germany and also the Director of the Research Institute on Nanocomposite Materials for Photonic Applications at Saint Petersburg State University in Russia. His main research topics include photocatalysis, photoelectrochemistry, solar chemistry and photochemistry focussed on the synthesis and the detailed investigation of the physical–chemical properties of semiconductor and metal nanoparticles. He holds an Honorary Professorship at the Robert Gordon University in Aberdeen/Scotland (United Kingdom), an Honorary Professorship at the Xinjiang Technical Institute of Physics and Chemistry (Chinese Academy of Sciences) in Urumqi (China), the Erudite Professorship at the Mahatma Gandhi University in Kottayam (India), a Guest Professorship of Tianjin University (China), a Visiting Professorship under the Academic Icon Programme at the University of Malaya (Malaysia), and is DeTao Master of Photocatalysis, Nanomaterials and Energy Applications (China). Prof. Bahnemann is the lead author of more than 290 publications in peer reviewed journals that have been cited more than 24,000 times (h-index: 60 according to ISI, 68 according to Google Scholar Citations) and has edited 4 scientific books.



Prof. Suresh C. Pillai was born in Karukachal, Kottayam, Kerala, India. He has completed his BSc and MSc (with first rank) from Mahatma Gandhi University, Kottayam. Suresh has obtained his PhD in the area of Nanotechnology from Trinity College (TCD), The University of Dublin, Ireland and then performed a postdoctoral research at California Institute of Technology (Caltech), USA. He has then worked at CREST in DIT as a senior scientist responsible for nanotechnology research before moving to Institute of Technology Sligo as a senior lecturer in environmental nanotechnology. He is an elected fellow of the Royal Microscopical Society (FRMS) and the Institute of Materials, Minerals and Mining (FIMMM). He is responsible for acquiring more than €3 million direct R&D funding. Prof. Pillai is a recipient of a number of awards for research accomplishments including the 'Industrial Technologies Award 2011' from Enterprise Ireland for commercialising nanomaterials for industrial applications. He was also the recipient of the 'Hothouse Commercialisation Award 2009' from the Minister of Science, Technology and Innovation and also the recipient of the 'Enterprise Ireland Research Commercialization Award 2009'. He has also been nominated for the 'One to Watch' award 2009 for commercialising R&D work (Enterprise Ireland). One of the nanomaterials based environmental technologies developed by his research team was selected to demonstrate as one of the fifty 'innovative technologies' (selected after screening over 450 nominations from EU) at the first Innovation Convention organised by the European Commission on 5–6th December 2011. He is the national delegate and technical expert for ISO standardization committee and European standardization (CEN) committee on photocatalytic materials.

1. Introduction

Photocatalysis refers to the acceleration of a chemical reaction in the presence of substances called photocatalysts, which can absorb light quanta of appropriate wavelengths depending on the band structure [1–4]. Usually semiconductors including TiO_2, Fe_2O_3, WO_3, ZnO, CeO_2, CdS, Fe_2O_3, ZnS, MoO_3, ZrO_2, and SnO_2 are selected as photocatalysts due to their narrow band gap and distinct electronic structure (unoccupied conduction band and occupied valence band) [5–24]. In semiconductor photocatalysis, electrons from the valence band of a semiconductor are excited to the conduction band by light of higher energy than the respective band gap, resulting in the formation of e^-_{CB}/h^+_{VB} pairs (Fig. 1). Conduction band electrons are good reducing agents (+0.5 to −1.5 V vs. NHE) whereas the valence band holes (h^+_{VB}) are strong oxidizing