Journal of Photochemistry and Photobiology C: Photochemistry Reviews 33 (2017) 132–164

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology C: Photochemistry Reviews

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

Review

# Inorganic semiconductors-graphene composites in photo(electro)catalysis: Synthetic strategies, interaction mechanisms and applications

Lütfiye Yıldız Ozer[a], Corrado Garlisi[a], Habeebllah Oladipo[a], Mario Pagliaro[b], Saad Asadullah Sharief[c], Ahmed Yusuf[a], Saif Almheiri[c], Giovanni Palmisano[a,*]

[a] Department of Chemical Engineering, Khalifa University of Science and Technology, Masdar Institute, Masdar City, PO BOX 54224, Abu Dhabi, United Arab Emirates
[b] Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy
[c] Department of Mechanical Engineering, Khalifa University of Science and Technology, Masdar Institute, Masdar City, PO BOX 54224, Abu Dhabi, United Arab Emirates

ARTICLE INFO

*Article history:*
Received 6 March 2017
Received in revised form 7 June 2017
Accepted 12 June 2017
Available online 15 June 2017

*Keywords:*
Photocatalysis
Photoelectrocatalysis
Inorganic semiconductors
Graphene
Composites

ABSTRACT

The remarkable physicochemical properties of graphene (GR) and derivatives can be leveraged in the photocatalytic activity of GR-semiconductor photocatalysts. The hitherto state of knowledge on the role of GR in these composite materials is insufficient and leaves many questions unanswered, thus it is imperative to fully understand the interaction mechanisms between GR and inorganic semiconductors. Detailed study and optimization of the features related to the interface are still very much sought to efficiently design photocatalysts targeting their eventual commercialization. This review shows that photocatalytic activity of such composites depends not only on high GR electron mobility and charge transfer, but also on the properties of the interface (such as interface morphology, size, crystal phases and facet, dimensionality of composites, etc.). Focusing on the last advancements in this field, this review analyses the challenges involved in the synthetic strategies of GR-semiconductor photo(electro)catalysts in various applications including pollutant degradation, organic synthesis, hydrogen evolution and photoreduction of carbon dioxide ($CO_2$). Mechanism of interaction between GR and semiconductors are thoroughly discussed by examining the proposed mechanism in the diverse areas where the composite materials are employed in photo(electro)catalytic processes. In addition, various synthetic and characterization technique available hitherto are presented, since they are pivotal to the understanding of the composites properties (such as morphology, crystal phases and exposed facets, degree of crystallinity, dimensionality etc.), and even to shed more light on interaction mechanisms of the photocatalyst constituents. As a future outlook, it is envisaged that research will not only focus on optimizing GR electrical and chemical properties, yet in the synthesis of GR-semiconductor photocatalysts attention needs also be placed on the properties of the resulting composites, using suitable synthetic methods and proper characterizations to assess their performance.

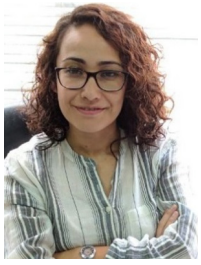


**Contents**



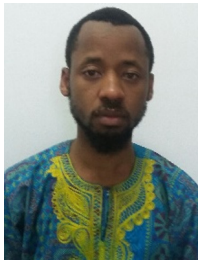
* Corresponding author.
*E-mail address:* gpalmisano@masdar.ac.ae (G. Palmisano).

https://doi.org/10.1016/j.jphotochemrev.2017.06.003
1389-5567/



**Lütfiye Yıldız Ozer** received her B.S in Biology (2008) and her M.S. in Biotechnology from Middle East Technical University (METU) (2011), Turkey. She worked as a research engineer under the supervision of Drs. Lina F. Yousef, Ahmed F. Yousef and currently of Dr. Giovanni Palmisano at the Masdar Institute (Khalifa University of Science and Technology) of Abu Dhabi (UAE). Her research interests mainly include the synthesis of reduced graphene oxide, the development and characterization of nitrogen doped $TiO_2$/graphene composites for hydrogen production from $H_2S$ splitting, and decontamination of greywater.

**Corrado Garlisi** is currently pursuing Doctoral Degree at Khalifa University of Science and Technology, Abu Dhabi (UAE). He earned his Master's Degree in Chemical Engineering from University of Palermo, Italy. Prior to joining Khalifa University of Science and Technology, he worked at ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development). His current research work focuses on the fabrication and characterization of semiconductor thin films for solar light activated glass.



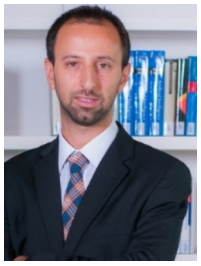
**Habeebllah Oladipo** received a B.S. in Chemical Engineering from Obafemi Awolowo University, Nigeria in 2011 and M.S. in Chemical Engineering from King Fahd University, Saudi-Arabia in 2016. He is presently a PhD student at Masdar Institute (Khalifa University of Science and Technology) under the supervision of Professor Giovanni Palmisano. His research interests include synthesis of nanostructured materials for clean fuel production and pollutant degradation.

**Mario Pagliaro** is a chemistry and energy scholar based at Italy's Research Council in Palermo where he leads a research Group focusing on nanochemistry, solar energy and the bioeconomy. In recognition of his "significant contributions to the chemical sciences" in 2014 he was designed Fellow of the Royal Society of Chemistry. The achievements of his Group's research developed in cooperation with leading researchers based in 20 countries include numerous important advances reported in over 180 research papers and several book chapters. He ranks amongst Italy's most cited scientists in nanotechnology and materials chemistry.

**Saad Asadullah Sharief** holds a Bachelor of technology (2012) from Jawaharlal Nehru technological University (India) and a Master of Science degree in Chemical Engineering (2015) from Masdar Institute. Following graduation, he joined the Electrochemistry Lab of Masdar Institute as a Research Engineer, where his work focused on electrochemical synthesis of graphene. His research interests mainly include large scale production of graphene, application of graphene in the realm of sensors-biosensors in particular and electrically conductive polymers.

**Ahmed Yusuf** received BS in Chemical Engineering from Obafemi Awolowo University, Nigeria in 2012, and Masters in chemical engineering from Masdar Institute, UAE in 2016 with research thesis titled "techno-economic evaluation of $CO_2$ utilization for Soda ash production using NaOH solution". He is currently a PhD student of Masdar Institute (Khalifa University of Science and Technology) under the supervision of Professor Giovanni Palmisano working on kinetic modelling of photocatalytic microreactor for water treatment applications and $H_2S$ splitting.

**Saif Almheiri** received his B.S. degree from the University of Arizona and M.S. and PhD degrees from the University of Miami, all in Mechanical Engineering. In 2014, he was a Visiting Assistant Professor at the Electrochemical Energy Laboratory at the Massachusetts Institute of Technology (MIT), where he worked on energy storage solutions. His research interests include energy storage, fuel cells for stationary and mobile applications, hydrogen production and synthesis of graphene and its applications.



**Giovanni Palmisano** is assistant professor of chemical engineering at the Masdar Institute (Khalifa University of Science and Technology) of Abu Dhabi (UAE). Giovanni's research activities have been developed in Italy, Spain and UAE and concern photo-catalytic processes for organic chemistry, hydrogen production, water and air remediation, self-cleaning coatings, and hybrid photovoltaics. From 2009–2012, he was administrator, chief engineer and safety manager at Hedera Engineering Srl – an Italian company operating in the field of solar energy plants. From 2008–2013 he has held free-lance consulting activity for private companies and Italian municipalities. He has co-authored ca. 80 journals papers and he has to his record six patents, six books and six invited book chapters.

## 1. Introduction

Rising concerns about global pollution and climate change due to ever increasing consumption of non-renewable, fossil hydrocarbons as fuels and chemical feedstocks [1] has made the development of green technologies for the production of goods [2] and the abatement of pollutants [3] the core of contemporary chemical research. Photocatalysis applied both to the degradation of organic and inorganic pollutants in water [4,5] and air [6,7], as well as to photoreduction of $CO_2$ [8,9], and hydrogen evolution [10–12], has emerged as a most promising method in our common path to sustainability.

Heterogeneous photocatalysis based on the utilization of semiconductors such as $TiO_2$ [13–17], CuO [18,19], ZnO [20,21], and $Fe_2O_3$ [22–24] to produce highly reactive radical species able to trigger oxidative reactions, as well as conduction band (CB) electrons promoting reduction conversions, presents many advantages, including low operation cost and no production of secondary hazardous metabolites. The open challenges before photocatalytic