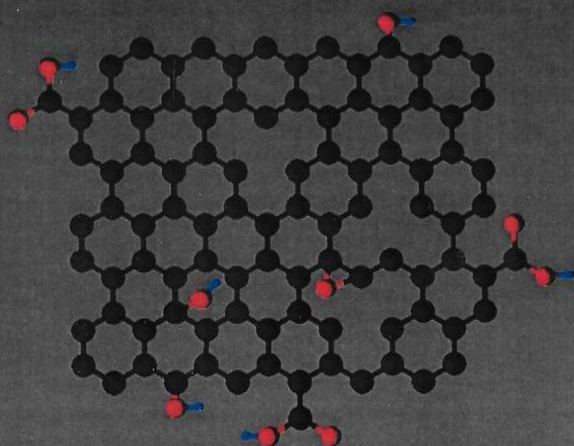


*Comprehensive Study in  
Recent Applications of Water  
Splitting Based on Modified  
Graphene Oxide*



**Mohammed Fathi Alsultan**

**Enas mohammed Hazim**

**Assim Adil Sabah**

---

# **Comprehensive Study in Recent Applications of Water Splitting Based on Modified Graphene Oxide**

**Mohammed Fathi Alsultan**

**Enas mohammed Hazim**

**Assim Adil Sabah**



## Table of contents

|                                                                                                                                  |     |
|----------------------------------------------------------------------------------------------------------------------------------|-----|
| Summary .....                                                                                                                    | VII |
| Introduction 1.1 .....                                                                                                           | 1   |
| -:Properties of Graphene Structure and 1.2 .....                                                                                 | 8   |
| -:production $H_2$ and $O_2$ Graphene as photocatalyst for $H_2$ 1.2.1 .....                                                     | 11  |
| -:Graphene as a channel for electron transfer 2 1.2 .....                                                                        | 20  |
| -:Graphene's role as a cocatalyst 1.2.3 .....                                                                                    | 32  |
| -:GO as redox mediator 1.2.4 .....                                                                                               | 36  |
| -:DSSC's based on graphene 1.2.5 .....                                                                                           | 39  |
| Graphene, semiconductors and A new approach for water splitting based on<br>Conductive polymers-Conductive polymers/or non ..... | 85  |
| :Concluding remarks 1.4 .....                                                                                                    | 88  |
| ncesRefere 1.5 .....                                                                                                             | 89  |

## Tables of Figures

|                                                                                                                                                                                                     |   |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| <i>Figure 1 Diagrammatic representation of the water splitting during natural photosynthesis and the conversion of energy from sun into carbohydrate and variety of living materials [9].</i> ..... | 2 |
| <i>Figure 2 Solar spectrum and maximum solar light conversion efficiencies for water splitting reactions with 100% quantum efficiency (Ref 12).</i> .....                                           | 4 |
| <i>Figure 3 Processes involved in overall photocatalytic water splitting on a semiconductor [Ref 13].</i> .....                                                                                     | 4 |

|                                                                                                                                                                                                                                                                          |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4 Energy diagram showing the conduction band and valance band potentials needed for a suitable photocatalytic water splitting system (Ref 27). .....                                                                                                              | 7  |
| Figure 5 (a) Energy band structure of pristine graphene with two cones touching at a Dirac point; energy band structure of b) n-type and c) p-type graphene with a bandgap(Ref. 31). .....                                                                               | 9  |
| Figure 6 Schematic structure illustrates the energy level diagram and the suggested mechanism for H <sub>2</sub> production (Ref.50). .....                                                                                                                              | 12 |
| Figure 7 (a) shows the amount of H <sub>2</sub> (μmol) per min. (b) shows H <sub>2</sub> evolution in (μmol) using 20% aqueous methanol solution per hour under UV-Vis irradiation(Ref 51). .....                                                                        | 13 |
| Figure 8 Illustrates the schematic structure of (a) the Ni/GO band gap structure and the photogenerated electron mechanism by Ni cocatalyst (b) hydrogen evolution mechanism from aqueous methanol solution under UV irradiation (Ref 51). .....                         | 13 |
| Figure 9 The NH <sub>3</sub> treatment along with heating repaired the vacancy-type defects in iGO-QDs through substitutional nitrogen doping, forming the quaternary nitrogen atoms in the iNGO-QDs(Ref 53). .....                                                      | 15 |
| Figure 10 wavelength absorption and H <sub>2</sub> and O <sub>2</sub> generation via iGO-QDs and iNGO-QDs. ....                                                                                                                                                          | 16 |
| Figure 11 Illustration of the preparation steps of PCN@N-graphene film(Ref 54) .....                                                                                                                                                                                     | 17 |
| Figure 12 The schematic representation of porous PCN@N-graphene film(Ref.54). ....                                                                                                                                                                                       | 18 |
| Figure 13(a) conceptual schematic of the NGO-QD structure. The main body of the NGO-QD consists of nitrogen-doped graphene layers stacked in the AB order, with the outer surface bore with oxygen functional groups. (b) Energy level diagrams of NGO-QDs(Ref 55) ..... | 19 |
| Figure 14 The configuration and energy diagram for NGO-QD photochemical diode (Ref 55) .....                                                                                                                                                                             | 20 |
| Figure 15 (a) Illustrates increasing current density with increase in calcinations temperature (versus potential RHE) of pristine iron oxide and                                                                                                                         |    |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |           |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <i>rGO/ g-Fe<sub>2</sub>O<sub>3</sub> samples at a scan rate of 20 mV s<sup>-1</sup> in 1.0 M NaOH electrolyte. (b) Schematic diagram of water splitting(Ref 57).....</i>                                                                                                                                                                                                                                                                                                                                                                                                                 | <i>21</i> |
| <i>Figure 16 Fig 15 a) Current density [J(mA cm<sup>-2</sup>)] vs V of NrGO (I), N/Co-doped PCP (II), N/Co-doped PCP//NrGO (III), and Pt/C and Pt/C (IV) at 5 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. b) LSV measurements of I, II, III, and IV at scan rate 5 mV s<sup>-1</sup> in 0.1 M KOH solution (Ref 63) .....</i>                                                                                                                                                                                                                                        | <i>24</i> |
| <i>Figure 17 (a) Schematic illustration of rGO–PDI-Co working principle. (b) Schematic representation of possible electron transfer processes in rGO–PDI-Co complex for photoelectrochemical hydrogen evolution reaction(67).....</i>                                                                                                                                                                                                                                                                                                                                                     | <i>26</i> |
| <i>Figure 18 (a) Illustration of the wide absorbance of Cu-Cu<sub>2</sub>O-graphene (b) graphical representation of amount of H<sub>2</sub> evolution per min(Ref 67)....</i>                                                                                                                                                                                                                                                                                                                                                                                                             | <i>27</i> |
| <i>Figure 19 Fig.18 Illustration of the proposed ‘two-way transfer’’ mechanism for hydrogen production with Cu–Cu<sub>2</sub>O–graphene(Ref.67). .....</i>                                                                                                                                                                                                                                                                                                                                                                                                                                | <i>28</i> |
| <i>Figure 20 mechanism of Cu/Cu<sub>2</sub>O/Graphene photocathode to produce H<sub>2</sub> and O<sub>2</sub>.....</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | <i>29</i> |
| <i>Figure 21 Illustration of the charge transfer in the MoS<sub>2</sub>/G-CdS composite under visible light irradiation. Graphene provides a template for photogenerated electron transfer (Ref 70).....</i>                                                                                                                                                                                                                                                                                                                                                                              | <i>31</i> |
| <i>Figure 22 The proposed mechanism for water splitting in BiVO<sub>4</sub>- rGO system(39) . .....</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | <i>32</i> |
| <i>Figure 23 (a) Influence of different graphene contents for P25–G photocatalysts (GP 0, GP 0.5, GP 1.5, GP 2.0, GP 2.5, GP 5.0 and G) on the amount of H<sub>2</sub> evolution in methanol aqueous solution under UV-vis irradiation using a 300 W high pressure Hg lamp[80].(b) The effect of different Cu contents in GP 2.0 photocatalysts on H<sub>2</sub> generation evolution in methanol aqueous solution under UV-vis light from a 300 W high pressure Hg lamp. (1) 0, (2) 0.5% Cu, (3) 1.0% Cu, (4) 1.5% Cu, (5) 2.0% Cu, (6) 3.0% Cu, (7) 5.0% Cu, (8) 8.0% Cu(71). .....</i> | <i>34</i> |
| <i>Figure 24 Schematic illustration of the charge transfer in TiO<sub>2</sub>/MG composites. The proposed mechanism for the enhanced electron transfer in the TiO<sub>2</sub>/MG system under irradiation assumes that the photoexcited electrons are transferred from the CB of TiO<sub>2</sub> not only to the MoS<sub>2</sub></i>                                                                                                                                                                                                                                                      |           |

|                                                                                                                                                                                                                                                  |           |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <i>nanosheets but also to the C atoms in the graphene sheets, which can effectively reduce <math>H^+</math> to produce <math>H_2</math> (72).....</i>                                                                                            | <i>36</i> |
| <i>Figure 25 Mechanism of water splitting in a Z-scheme photocatalysis system consisting of Ru/SrTiO<sub>3</sub>: Rh and PrGO/BiVO<sub>4</sub> under visible-light irradiation (40).....</i>                                                     | <i>38</i> |
| <i>Figure 26 The energy level diagram for <math>H_2</math> evolution over EY-rGO/Pt photocatalyst;(b)The proposed photocatalytic mechanism for hydrogen evolution over EY-rGO/Pt photocatalyst under visible light irradiation(Ref 75) .....</i> | <i>40</i> |
| <i>Figure 27 Proposed mechanism for <math>H_2</math> generation[177].....</i>                                                                                                                                                                    | <i>87</i> |
| <i>Figure 28 Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts.....</i>                                                                                                           | <i>89</i> |

## Table

|                                                                                                                                                                                                                                                                                                                  |           |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <i>Table 1 Developments in the graphene based photocatalysts system – the role of graphene / graphene oxide, type of photocatalysts for <math>H_2</math> and / or <math>O_2</math> evolution, operating conditions, significant results such as photocurrent density, IPCE and corresponding references.....</i> | <i>41</i> |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|

---

## *Acknowledgment*

This book has been analysed scientifically and thoroughly over 200 recent publications that highlighted water splitting based on reduced graphene oxide as renewable energy. We thank prof. Gerhard Swiggers from Wollongong University who provide us with most of these references and highlighted the interesting results of them. We thank University of Mosul that supported us over the last few months and provide us with all logistic facilities.

## Authors

### Mohammed Fathi Alsultan

- Bachelor in Science (B.S.) Chemistry University of Mosul/Iraq in 2001
- Master in Education (M.S.E) CHEMISTRY University of Mosul/Iraq in 2006
- Doctor of Philosophy (Ph.D.) Chemistry University of Wollongong / Australia in 2019
- Chemistry Lecture at University of Mosul basic education collage science 2007.
- Inorganic, Organic and Biochemistry since 2007 till now. More than 12 publication since 2016 in different international Journal.
- Email [mohamadfkaleel@uomosul.edu.iq](mailto:mohamadfkaleel@uomosul.edu.iq)



### Enas Hazim Mohammed

- Bachelor in Science (B.S.) Chemistry University of Mosul/Iraq in 1996
- Master in Education (M.S.i) CHEMISTRY University of Mosul/Iraq in 2005
- Doctor of Philosophy (Ph.D.) Department of Chemistry/ College of Science / University of Mosul/ Iraq 2010
- Chemistry lecture at University of Mosul basic education collage science since 2010.
- Lecture asst. at University of Mosul pharmacy collage (1997-2010)
- Lecture at University of Mosul basic education collage (2010-till present) Email: [enashazim@uomosul.edu.iq](mailto:enashazim@uomosul.edu.iq)



### Assim Adil Sabah

- Bachelor in Science (B.S.) Chemistry University of Mosul/Iraq in 2005
- Master in Education (M.S.i) CHEMISTRY University of Mosul/Iraq in 2007
- Doctor of Philosophy (Ph.D.) Department of Chemistry/ College of Science / University of Mosul/ Iraq 2011.
- Chemistry Asst. Prof. at University of Mosul basic education collage science 2017.
- The editor of basic education journal (2017,2018). - The head of science dept. (2018-present).
- Email: [assimsabah@uomosul.edu.iq](mailto:assimsabah@uomosul.edu.iq)



## Summary

Currently, alternative energy being the most attractive technology demands around the world, due to an increase consumption of fossil oil. In contrast, fossil oil itself is depleting source of energy causes high amount of CO<sub>2</sub> emissions. Which leads to damage environments as a results of greenhouse phenomenon. Renewable energy is other term of alternative energy includes of exploiting natural power that come from sun, wind, geothermal heat, and nuclear energy. Water splitting is another type of renewable clean energy. In the last decades thousands of studies have focused on this sort of energy. This is because water splitting is cheap, environment friendly, could has high efficiency with long term of durability. In this book we highlighted the actual roles of reduced graphene oxide (rGO) in water splitting system. Over of two hundred references have analyzed and discussed thoroughly. Firstly in the introduction explained the water system principles and rGO chemical and physical properties. Then we addressed the roles of rGO in water splitting system. We concluded that rGO can play as photocatalyst, electron transfer channel, as cocatalyst, as redox mediator, dye-sensitized solar cell (DSSC).

## 1.1 Introduction

In 2008, the total energy consumption was estimated to be about 17 terawatts and it has been predicted to be double by 2050 and triple by 2100. Currently, 80 % of world's total energy consumption depends on fossil fuel which includes oil, natural gas and coal. Fossil fuel is depleting source of energy and the burning of it causes CO<sub>2</sub> emission which directly affects the change in climatic conditions. Thus, it is a necessity now to find a new alternative source for energy to reduce the dependence on fossil fuel and this could be achieved by other sources of energy such as biomass, nuclear, wind, geothermal energy and solar cell. Among them, it appears that, solar cell is the best choice. This is because each of the other resources has negative impacts either on the environment or in utilizing them. For example, biomass causes CO<sub>2</sub> emission; nuclear power has radioactive waste which has longer half-lives and there are always safety concerns associated with it (e.g., Chernobyl and Fukushima nuclear incidents) and finally when it comes to wind and geothermal energy sources, both have low efficiency and high cost of production<sup>1</sup>.

Solar cell is a promising alternative technology because it is clean and green energy and it is able to alleviate energy crisis and environmental pollution. Many research papers and review articles are dedicated to this topic over the past few years. It is now known that solar energy that is received on the Earth's surface could meet the current and future human energy demand<sup>2-4</sup>. For example, when the sun light hits our planet for one hour it is equivalent to the total amount of energy that is consumed by all human activities in an year. It is anticipated that solar energy conversion system is estimated to contribute around 5% of global electricity consumption by 2030, and 11% by 2050<sup>5</sup>. This also means that avoiding 2.3 gigatonnes (Gt) of CO<sub>2</sub> emissions

collectors through employing the sun's thermal energy and solar driven water-splitting (also known as artificial photosynthesis)<sup>8-9</sup>

In natural photosynthesis, sun, water and light are those needed for the plants to capture and convert sunlight into carbohydrates ( $C_xH_{2x}O_x$ ) and other organic molecules which make up living organisms (biomass) and the food that we eat. The cycle of the natural photosynthetic activity has been in these plants from millions of years ago. It could be suggested that the origin of coal, which is the major form of fossil oil, is the plant itself after exposed to high temperature and pressure. Fig 1 illustrates the principles of energy flow in biology<sup>9</sup>.

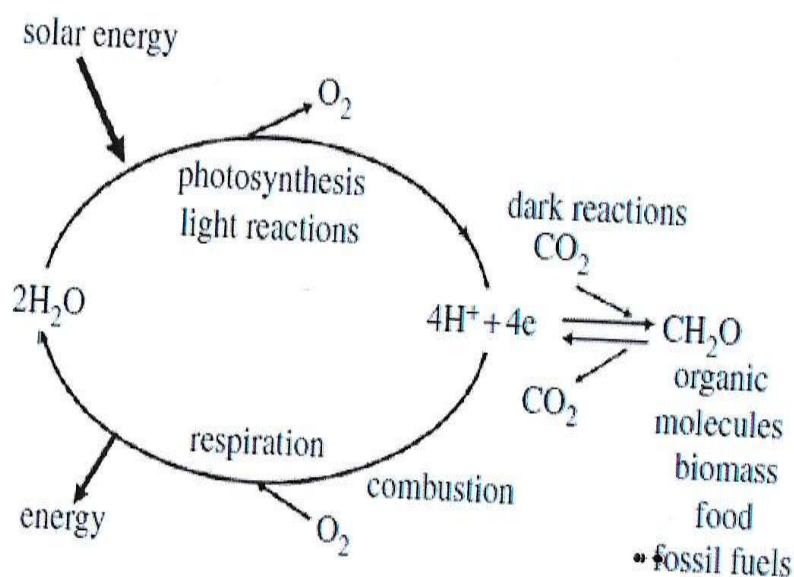


Figure 1 Diagrammatic representation of the water splitting during natural photosynthesis and the conversion of energy from sun into carbohydrate and variety of living materials [9].

### **Mohammed Fathi Alsultan**

- *Bachelor in Science (B.S.) Chemistry University of Mosul/Iraq in 2001*
- *Master in Education (M.S.E) CHEMISTRY University of Mosul/Iraq in 2006*
- *Doctor of Philosophy (Ph.D.) Chemistry University of Wollongong / Australia in 2019*
- *Chemistry Lecture at University of Mosul basic education collage science 2007*
- *Inorganic, Organic and Biochemistry since 2007 till now. More than 12 publication since 2016 in different international Journal.*

### **Enas Hazim Mohammed**

- *Bachelor in Science (B.S.) Chemistry University of Mosul/ Iraq in 1996*
- *Master in Education (M.S.i) CHEMISTRY University of Mosul/ Iraq in 2005*
- *Doctor of Philosophy (Ph.D.) Dept. of Chemistry/ College of Science / University of Mosul/ Iraq 2010*
- *Chemistry lecture at University of Mosul basic education collage science since 2010.*
- *Lecture Asst. at University of Mosul pharmacy collage (1997 - 2010)*
- *Lecture at University of Mosul basic education collage (2010-till present)*

### **Assim Adil Sabah**

- *Bachelor in Science (B.S.) Chemistry University of Mosul/ Iraq in 2005*
- *Master in Education (M.S.i) CHEMISTRY University of Mosul/Iraq in 2007*
- *Doctor of Philosophy (Ph.D.) Department of Chemistry/ College of Science / University of Mosul/ Iraq 2011.*
- *Chemistry Asst. Prof. at University of Mosul basic education collage science 2017.*
- *The editor of basic education journal (2017,2018).*
- *The head of science dept. (2018-present).*

ISBN 9789922970684



9 789922 970684