

Reduction Band Gap Energy of TiO₂ Assembled with Graphene Oxide Nanosheets

Abdelmajid Timoumi^{1,2}

¹Physics Department, Faculty of Applied Science, Umm AL-Qura University, Makkah, KSA

²Photovoltaic and Materials Semiconductors Laboratory, National Engineering School of Tunis, Tunis, Tunisia

Email: timoumiabdelmajid@yahoo.fr

How to cite this paper: Timoumi, A. (2018) Reduction Band Gap Energy of TiO₂ Assembled with Graphene Oxide Nanosheets. *Graphene*, 7, 31-38.
<https://doi.org/10.4236/graphene.2018.74004>

Received: September 22, 2018

Accepted: October 28, 2018

Published: October 31, 2018

Copyright © 2018 by author and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

This research work aims to reduce the band gap of thin layers of titanium oxide by the incorporation of graphene oxide sheets. Thin layers of the TiO₂-GO composites were prepared on a glass substrate by the spin-coating technique from GO and an aqueous solution of TiO₂. A significant decrease in optical band gap was observed at the TiO₂-GO compound compared to that of pure TiO₂. Samples as prepared were characterized using XRD, SEM and UV-visible spectra. XRD analysis revealed the amorphous nature of the deposited layers. Scanning electron microscope reveals the dispersion of graphene nanofiles among titanium oxide nanoparticles distributed at the surface with an almost uniform size distribution. The band gap has been calculated and is around 2 eV after incorporation of Graphene oxide. The chemical bond C-Ti between the titanium oxide and graphene sheets is at the origin of this reduction.

Keywords

Titanium (IV) Oxide, Graphene Oxide, TiO₂-GO, Thin Films, Composite Materials

1. Introduction

The Titania, existing in rutile or anatase phase, is considered an important material for different applications because of its characteristic of photoexcitation phenomenon. Among the applications, the efficiency of photovoltaic solar cells and photocatalytic devices could be improved if the band gap of titanium oxide layers could be reduced [1] [2]. Titanium oxide (TiO₂) has excellent chemical stability, mechanical hardness and optical transmittance with high refractive index. It has attracted great attention these years and it is widely used in solar cells

[3] and other areas.

Originally, the Titania has a band gap more than 3 eV. The lowering of the band gap is essential for optimal use of sunlight and therefore for improving the efficiency of the devices thus produced. A Graphene oxide (GO) is explored for its important effect on the band gap of titanium thin layers. In this context, the composites of GO and TiO₂ are highly promising. There are many reports on the preparation of graphene-TiO₂ composite [4] and its application in the dye-sensitized solar cell [5]. In fact, several studies have been reported in the literature [6] [7] [8] in order to reduce the band gap of TiO₂.

TiO₂ thin films can be prepared by different techniques such as sputter depositions [9], sol-gel process [10], chemical vapour deposition (CVD) [11], and ion beam-assisted processes [12]. In this investigation spin coating technique was used for the deposition of TiO₂ thin films. TiO₂-Graphene oxide composite was successfully prepared via a simple coating approach. Structural, morphological, and optical properties of obtained layers were studied and well discussed in this work. The optical properties give information regarding the band gap Eg, the refractive index *n* and the extinction coefficient *k*.

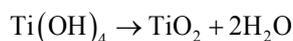
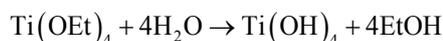
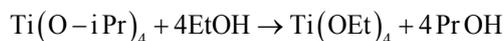
2. Experimental

2.1. Materials

The Titanium (IV) Isopropoxide (TIP) (99.999%), the graphene oxide in powder form (4% - 10% edge-oxidized) and other chemical reagent were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used as-received.

2.2. Preparation of TiO₂-Graphene Oxide

At room temperature the Titanium isopropoxide (TIP) (precursor) was mixed with acetic acid (stabilizer) and ethanol (solvent) in the molar ratio TIP: ethanol: acetic acid = 1:0.1:9. Then, the resulting solution form was stirred during 2 h. The reaction mechanism for TiO₂ formation is:



On the other hand the Graphene oxide solution was prepared separately by dispersing graphene oxide (sheets) in powder form in 5 ml of ethanol. After that it is sonicated for 20 minutes. The mass of GO dispersed and mixed with TiO₂ solution is 15 mg. The mixture of TiO₂ and Graphene oxide solutions (5:1) were used and stirred for 30 minutes. Finally, the solution containing TiO₂-Graphene oxide composite is obtained. A spin coating (Model WS-650MZ-23NPPB) was performed in air by flooding the substrate surface (glass substrate) with spinning at 3500 r/min for 30 s. Thin homogenous layers of TiO₂-GO with 250 nm thickness were obtained.

2.3. Characterization Methods

A shimadzu type XRD-6000 X-ray diffractometer with a Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) were used for X-ray diffraction analysis. The morphologies of the samples were examined by scanning electron microscopy (SEM, Shimadzu Supers can SSX-550). A spectrophotometer with a resolution of 0.1 nm (Shimadzu 3150 UV-VIS-NIR) were used for the measurement of the transmittance spectra $T(\lambda)$ and the reflectance $R(\lambda)$ of the layers under a normal incidence at room temperature in the spectral range (200 - 1800 nm). The thickness layer was determined by a stylus displacement of a Veeco Dektak 150 profilometer.

3. Results and Discussions

3.1. XRD Analysis

The crystal structure of TiO₂ and TiO₂-GO samples obtained by XRD is shown in **Figure 1**. The XRD pattern for the samples showed no detectable peaks, indicating that the samples were amorphous. The possible reason is either to organic solvents which inhibited the formation of the crystalline structure of TiO₂ [13], or to the low calcination temperature given during the growth of TiO₂ thin layers [14] [15]. Complete transformation of brookite to anatase was achieved at a calcination temperature of 400°C [16]. No characteristic diffraction peaks for Graphene oxide are observed because it's relatively low diffraction intensity and the low amount used.

3.2. SEM Analysis

Figure 2 shows the images of as-prepared TiO₂ and TiO₂-GO samples obtained with scanning electron microscope and scanned with 10,000 magnifications. The titanium oxide product film has homogeneity of the nanoparticles to appreciable dimensions. Agglomerated nanoparticles and pinholes have also been observed on the film. The film also shows a basic morphology of semi-spherical grains with random formation in the shape of a flower. The surface morphology of the

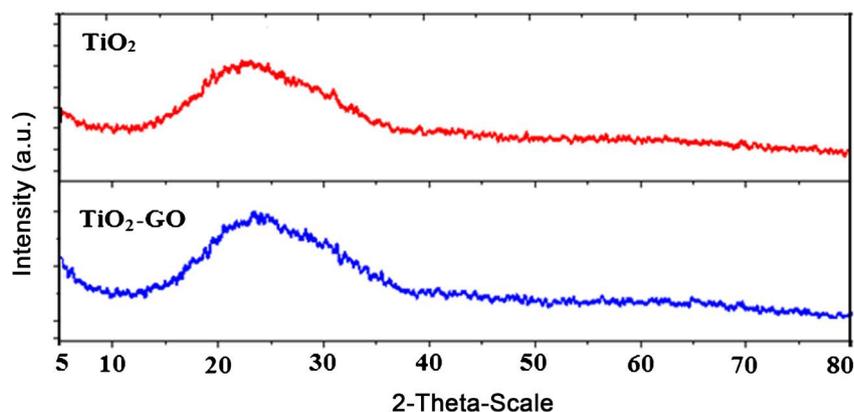


Figure 1. X ray diffraction patterns of TiO₂ and TiGO samples synthesized by spin coating.

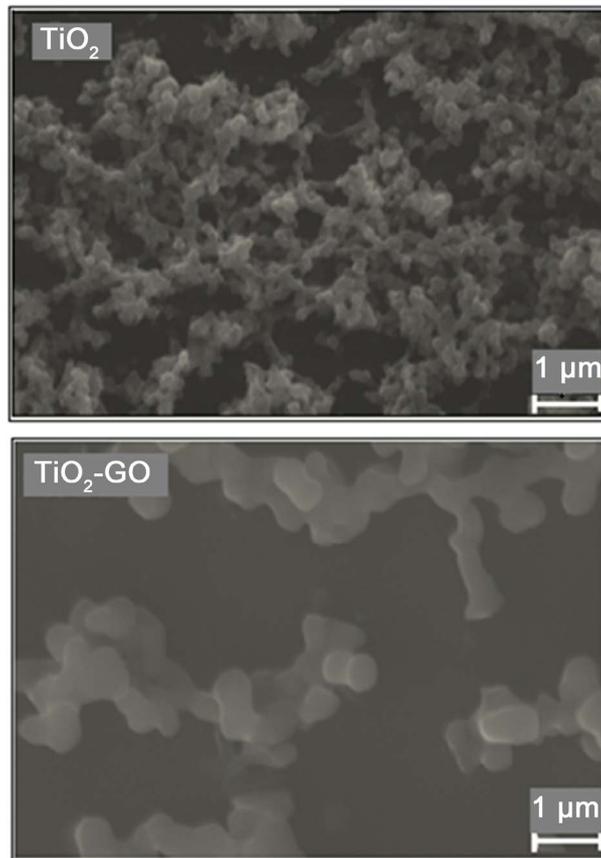


Figure 2. SEM patterns of TiO_2 and TiO_2 -GO samples synthesized by spin coating.

TiO_2 -GO composite shows a spherical/rod-like distribution of TiGO and partially agglomerated at the surface. Thus, the TiO_2 spheres were practically supported on the surface of the graphene oxide sheets and combined with each other.

3.3. Optical Measurements

Figure 3(a) depicts the transmission T and the reflection R spectra as a function of wavelength for TiO_2 and TiO_2 -GO samples. These layers exhibited good transparency in the infrared region. A decrease in both R and T values which attributed to GO particles is distributed in the total matrix volume [17] is noted. **Figure 3(b)** describes the variation between $(ah\nu)^2$ and photon energy (eV), which shows that the band gap of pure TiO_2 is about 3.67 eV; value in accordance to the literature [18], whereas the band gap obtained of the TiO_2 -GO composite has been reduced to 2.0 eV. This value is interesting for large spectra photon absorption [19]. This, shows that the addition of graphene oxide particles effectively increases the visible light absorption capacity of the titanium dioxide thin layer [8]. This can be explained by the presence of acids and oxidizing agents in the synthesis solution. Many groups containing oxygen, such as hydroxyl (C-OH), carboxyl (C-OH) and epoxy (C-O-C) groups become covalently bonded to surfaces of Graphene oxide sheets. So, in the presence of some functional group such as (-OH) and (-COOH) Graphene oxide reacted. Some

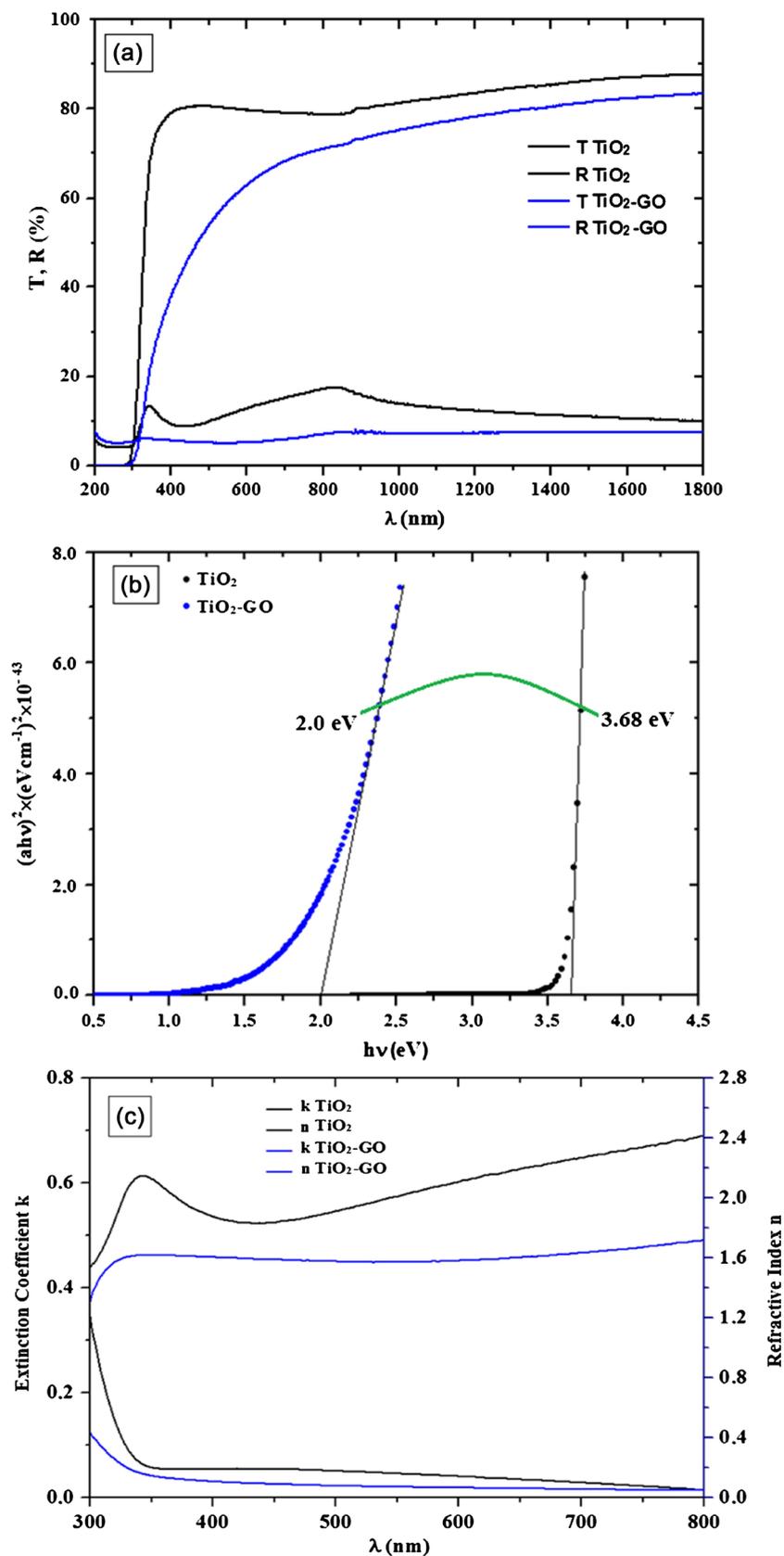


Figure 3. (a) Transmission and reflection of samples; (b) Band gap energy ($h\nu$) of TiO₂ and TiO₂-GO composites; and (c) Refractive index n and Extinction coefficient k spectra of TiO₂ and TiO₂-GO samples.

unpaired Π -electrons bonded with the free electrons on the surface of TiO_2 forms a Ti-O-C structure, which shifted up the valence band edge and reduce the band gap. In addition, we can suppose that formed C-Ti bond can also participate in the reduction of the band gap of TiO_2 .

Figure 3(c) grouped the variation of extinction coefficient and refractive index of samples. The refractive index n , was determined using the reflection, R , values from equation above according to:

$$n = \frac{1 + R^2}{(1 - R)^2} + \frac{\sqrt{4R - (1 - R)^2} k^2}{(1 - R)}$$

Here, R is the reflectance value, ($k = \alpha\lambda/4\pi$) is the extinction coefficient.

The values of the refractive index n , rise in the Ultraviolet spectral range for samples. The n values shifted to longer UV wavelengths when GO is added to TiO_2 . This could be attributed to the fact of the GO that introduced in the solution which may increase density, leading to an increase of n values. The extinction coefficient, k , indicates that high values are indicated in the zone of the strong absorption or the extrinsic absorption, and decreases in the zone of the weak absorption.

The mechanism diagram showing this process is given in **Figure 4**. Under light irradiation, electrons were excited from the valence band to the conduction band of TiO_2 , leaving positively charged holes in the valence band. In the absence of acceptor, the recombination of electrons and positive charges would take place. A C-Ti bond will be formed participating in the reduce of the TiO_2 band gap.

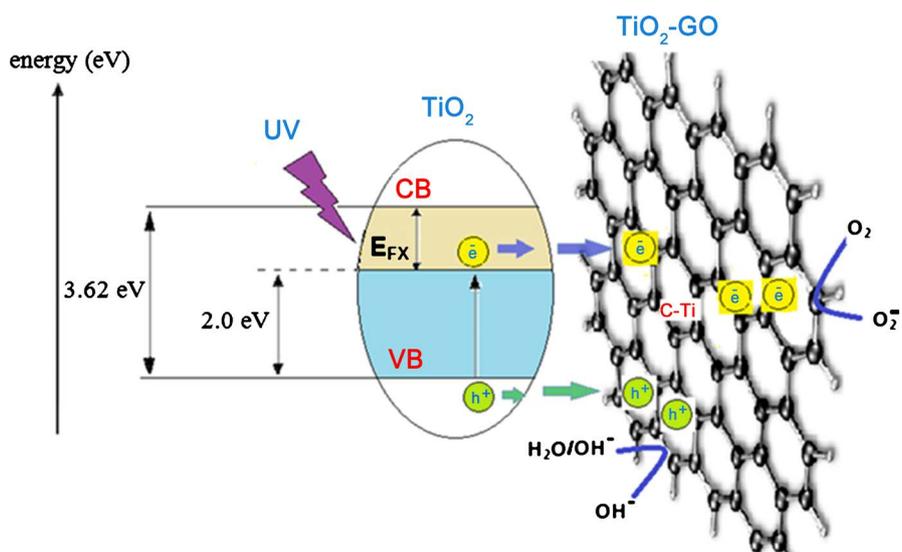


Figure 4. Schematic illustrating the charge transfer in the TiO_2 -GO composite under visible light irradiation with a new energy level E_{FX} .

4. Conclusion

In this study, TiO_2 -GO composite thin layers were synthesized by a spin coating

ethod. The dispersion of graphene oxide nanosheets in TiO₂ thin layers, crystallinity, morphology and band gap was evaluated. It was revealed by scanning electron microscopy that the deposited layers are detected some aggregates. The band gap obtained of TiO₂-GO composite thin layer was 2 eV as compared to pure titania thin film. This result is significant and encouraging for various applications in different fields, such as dye-sensitive solar cells.

Acknowledgements

The author would like to thank King Abdulaziz City of Science and Technology (KACST) for the financial support (Project number: 125-37).

The author also thanks Prof. S. N. Alamri from the Taibah University, Madinah, KSA for samples characterizations.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

- [1] Linsebigler, A.L., Lu, G. and Yates, J.T. (1995) Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Journal Chemical Reviews*, **95**, 735-758. <https://doi.org/10.1021/cr00035a013>
- [2] O'Regan, B. and Gratzel, M. (1991) A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. *Nature*, **353**, 737-740. <https://doi.org/10.1038/353737a0>
- [3] Adachi, M., Murata, Y., Takao, J., Jui, J.T., Sakamoto, M. and Wang, F.M. (2004) Highly Efficient Dye-Sensitized Solar Cells with a Titania Thin-Film Electrode Composed of a Network Structure of Single Crystal-Like TiO₂ Nanowires Made by the "Oriented Attachment" Mechanism. *Journal of the American Chemical Society*, **126**, 14943-14949. <https://doi.org/10.1021/ja048068s>
- [4] Zhu, C., Guo, S., Wang, P., Xing, L., Fang, Y., Zhai, Y. and Dong, S. (2010) One-Pot, Water-Phase Approach to High-Quality Graphene/TiO₂ Composite Nanosheets. *Chemical Communications*, **46**, 7148-7150. <https://doi.org/10.1039/c0cc01459a>
- [5] Tang, Y.B., Lee, C.S., Xu, J., Liu, Z.T., Chen, Z.H., He, Z., Cao, Y.L., Yuan, G., Sang, H., Chen, L. Luo, L., Cheng, H.M., Zhang, W.J., Bello, I. and Lee, S.T. (2010) Incorporation of Graphenes in Nanostructured TiO₂ Films via Molecular Grafting for Dye-Sensitized Solar Cell Application. *ACS Nano*, **4**, 3482-3488. <https://doi.org/10.1021/nn100449w>
- [6] Chen, X. and Mao, S.S. (2007) Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical Reviews*, **107**, 2891-2959. <https://doi.org/10.1021/cr0500535>
- [7] Liu, G., Wang, L., Yang, H.G., Cheng, H.M. and Lu, G.Q. (2010) Titania-Based Photocatalysts-Crystal Growth, Doping and Heterostructuring. *Journal of Material Chemistry*, **20**, 831-843. <https://doi.org/10.1039/B909930A>
- [8] Zhang, Y. and Pan, C. (2011) TiO₂/Graphene Composite from Thermal Reaction of Graphene Oxide and Its Photocatalytic Activity in Visible Light. *Journal of Materials Science*, **46**, 2622-2626. <https://doi.org/10.1007/s10853-010-5116-x>

- [9] Sellappan, R., Sun, J., Galeckas, A., Lindvall, N., Yurgens, A., Kuznetsov, A.Y. and Charkarov, D. (2013) Influence of Graphene Synthesizing Techniques on the Photocatalytic Performance of Graphene-TiO₂ Nanocomposites. *Physical Chemistry*, **15**, 15528-15537.
- [10] Ishibashi, K., Nosaka, Y., Hashimoto K. and Fujishima, A. (1998) Time-Dependent Behavior of Active Oxygen Species Formed on Photo-Irradiated TiO₂ Films in Air. *The Journal of Physical Chemistry B*, **102**, 2117-2120.
<https://doi.org/10.1021/jp973401i>
- [11] Zhao, Q.N., Li, C.L. and Zhao, X.J. (2003) The Structure and Photocatalytic Activity of CeO₂ Doped TiO₂ Films Deposited on Glass by Magnetron Sputtering. *Key Engineering Materials*, **249**, 451-456.
<https://doi.org/10.4028/www.scientific.net/KEM.249.451>
- [12] Gilo, M., and Croitoru, N. (1996) Properties of TiO₂ Films Prepared by Ion-Assisted Deposition Using a Gridless End-Hall Ion Source. *Thin Solid Films*, **283**, 84-89.
[https://doi.org/10.1016/0040-6090\(95\)08500-9](https://doi.org/10.1016/0040-6090(95)08500-9)
- [13] Ota, M., Dwijaya, B., Hirota, Y., Uchida, Y., Tanaka, S. and Nishiyama, N. (2016) Synthesis of Amorphous TiO₂ Nanoparticles with a High Surface Area and Their Transformation to Li₄Ti₅O₁₂ Nanoparticles. *Chemistry Letters*, **45**, 1285-1287.
<https://doi.org/10.1246/cl.160702>
- [14] Paola, A.D., Bellardita, M. and Palmisano, L. (2013) Brookite, the Least Known TiO₂ Photocatalyst. *Catalysts*, **3**, 36-73. <https://doi.org/10.3390/catal3010036>
- [15] Li, J.G., Ishigaki, T. and Sun, X. (2007) Anatase, Brookite, and Rutile Nanocrystals via Redox Reactions under Mild Hydrothermal Conditions: Phase-Selective Synthesis and Physicochemical Properties. *The Journal of Physical Chemistry C*, **111**, 4969-4976. <https://doi.org/10.1021/jp0673258>
- [16] Mothi, K.M., Soumya, G. and Sugunan, S. (2014) Effect of Calcination Temperature on Surface Morphology and Photocatalytic Activity in TiO₂ Thin Films Prepared by Spin Coating Technique. *Bulletin of Chemical Reaction Engineering & Catalysis*, **9**, 175-181. <https://doi.org/10.9767/bcrec.9.3.5733.175-181>
- [17] Timoumi, A., Alamri, S.N. and Alamri, H. (2018) The Development of TiO₂-Graphene Oxide Nano Composite Thin Films for Solar Cells. *Results in Physics*, **11**, 46-51. <https://doi.org/10.1016/j.rinp.2018.06.017>
- [18] Khan, M.I., Bhatti, K.A., Qindeel, R., Althobaiti, H.S. and Alonizan, N. (2017) Structural, Electrical and Optical Properties of Multilayer TiO₂ Thin Films Deposited by Sol-Gel Spin Coating. *Results in Physics*, **7**, 1437-1439.
<https://doi.org/10.1016/j.rinp.2017.03.023>
- [19] Štengl, V., Bakardjieva, S., Grygar, T.M., Bludská, J. and Kormunda, M. (2013) TiO₂-Graphene Oxide Nanocomposite as Advanced Photocatalytic Materials. *Chemistry Central Journal*, **7**, 41. <https://doi.org/10.1186/1752-153X-7-41>