Enhanced Photocatalytic Activity of ZnO Nanorods/(Graphene Oxide, Reduced Graphene Oxide) for Degradation of Methyl Orange Dye

Luis A. Sánchez*, Brian E. Huayta¹, Pierre G. Ramos¹ and Juan M. Rodriguez¹
¹Center for the Development of Advanced Materials and Nanotechnology, Universidad Nacional de Ingeniería, Perú.

* lsanchez@uni.edu.pe

Abstract: ZnO has been well-known as a significant photocatalyst material due to its high surface area, efficient charge transport, and superior photosensitivity. Even though photocatalysis using bare ZnO NRs is useful in pollutant remediation, two main drawbacks scale down their performance as photocatalysts. First, ZnO NRs absorb mainly the UV light, which compromises a small portion of the solar spectrum, and second, the high recombination rate in the ZnO NRs prevents the path of electron-hole outward and then reduces the photocatalysis efficiency. In this work, ZnO-NRs, ZnO-NRs/Graphene Oxide (GO), and ZnO-NRs/Reduced Graphene Oxide (rGO) array composites were vertically grown on conductive glass substrates of SnO₂:F (FTO). The films were synthesized by hydrothermal method using ZnO seed layers deposited by spray pyrolysis technique. The nanosheets of GO and rGO were anchored onto the surface of the as-prepared ZnO-NRs by using the spray deposition technique (SDT). The photocatalytic activity of these materials was studied by analyzing the degradation of methylene orange (MO) in an aqueous solution under ultraviolet light, and we found that the decoration of ZnO-NRs with nanosheets of GO and rGO resulted in a significant enhancement of the photocatalytic degradation efficiency, where ZnO-NRs/rGO are more efficient than ZnO-NRs/GO and the latter better than pure ZnO-NRs.

1. Introduction
Over the past few decades, organic dyes have been extensively produced and applied in several industries, including textile, leather, pulp and paper production, food processing, and pharmaceuticals [1]. However, it is widely recognized that the dyes cause some serious problems to aquatic environments and human health disorders [2]. Therefore, these concerns have led to developing more efficient treatment technologies for the removal of colored organic dyes from wastes. Various methods to handle the removal of organic dyes from water have been developed, such as biodegradation [3], adsorption [4], coagulation [5], and advanced oxidation processes (AOPs) [6]. Particularly, Advanced Oxidation Processes, based on the generation of hydroxyl radicals and other reactive species for environmental remediation, have been successfully deployed for the treatment of a broad range of organic dyes pollutants [7]. Among AOPs, heterogeneous photocatalysis, which is a promising, simple, and eco-friendly technology, appears as the most emerging destructive treatment [8]. This process uses semiconductors nanomaterial as photocatalysts due to their lower cost, non-toxicity, and size-tunable physicochemical properties [9,10], highlighting particularly zinc oxide (ZnO) which has been proven to have a high photocatalytic degradation efficiency [11]. However, attempts for the application of pristine ZnO as a photocatalyst faces some obstacles, such as its low activity in visible light (~43% of solar spectrum) [12] and its fast recombination of photogenerated electron-hole (e-/-h+) pairs. Therefore, strategies like doping the ZnO nanorods with metals or nonmetals elements, combining with other materials, and coupling with carbon-based materials [13-15] have been adopted to solve these issues and improve its dye degradation efficiency. Among the carbon materials, graphene oxide (GO) and reduced graphene oxide (rGO) have become promising materials due to their unique two-dimensional (2D) structure, high electron conductivity and mobility, and high surface area [14]. Currently, ZnO/GO and ZnO/rGO nanorods films have also
attracted research attention in recent years since offering new opportunities in photocatalysis as proved by several studies [16-18].

Herein, ZnO/GO and ZnO/rGO nanorods were fabricated on fluorine-doped tin oxide (FTO) glass substrates via the combination of seed layers-low temperature hydrothermal growth for the formation of ZnO nanorods. The GO and rGO sheets were deposited on the surface of hydrothermally synthesized ZnO nanorod films by spray deposition technique controlling the amount of GO and rGO sheets deposited on the films. Furthermore, we determined the effect of GO and rGO content on the morphology, crystallinity, optical and photocatalytic properties of the obtained ZnO/GO and ZnO/rGO nanorods. Detailed morphological, structural, and optical characterization of the obtained films were investigated by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and Raman spectroscopy. Finally, the photocatalytic methyl orange (MO) degradation performances of the samples under UV radiation were investigated.

2. Experimental procedures

ZnO-NRs, ZnO-NRs/GO, and ZnO-NRs/rGO composites films were fabricated on conductive glass substrates of SnO$_2$: F (FTO). The films were synthesized by a three steps method: first, ZnO seed layers were deposited by spray pyrolysis technique on FTO substrates. The second step was the growth of nanorods in a supersaturated solution of zinc nitrate and hexamethylenetetramine (HMT) at 90$^\circ$C from the deposited seeds. Finally, nanosheets of GO and rGO were anchored onto the surface of the as-prepared ZnO-NRs by using the spray deposition technique.

FTO conductive glass (Libbey Owens Ford glass substrates coated with a layer of transparent and conducting SnO$_2$:F having a resistance of 8 Ω/cm$^2$) was used as the substrate for the growth of ZnO nanorods and the composite films. In practice, 2.0 × 1.5 cm$^2$ pieces of FTO conductive glass were cleaned in an ultrasonic bath, first with water and then with ethanol, before depositing the seed layer.

2.1. Seed deposition

Zinc oxide seed films were first deposited onto the pre-cleaned FTO-coated glass substrate using the spray pyrolysis (SP) technique and were then subsequently used as the substrate to grow ZnO nanorods [19].

In a homemade SP technique described in detail elsewhere [19], a medical nebulizer was used as an atomizer to produce uniform size droplets which were directed by a nozzle towards the hot substrate (350 $^\circ$C). The nozzle performed an oscillating movement at constant velocity to scan the whole area of the substrate. The average distance between the nozzle distance and the substrate is 5 mm. The precursor used in all experiments for the present work was a 0.10 M zinc acetate solution (Riedel-de-Haen, Seelze, Germany) in deionized water. Some drops of acetic acid were added to ensure both the total dissolution of zinc acetate and to adjust the pH of the precursor solution to 5. Micro-filtered air was used as a carrier gas at a fixed pressure of 2 × 10$^5$ Pa with a gas flow maintained at 15 L/min.

2.2. Growth of ZnO NRs films

The solution medium used for the growth of the ZnO NRs was prepared as follows: equal volumes of zinc nitrate [Zn(NO$_3$)$_2$·6H$_2$O] (0.1 M), ammonium acetate [CH$_3$COONH$_4$] (0.1 M) and hexamethylenetetramine [C$_6$H$_2$N$_4$] (0.1 M) were mixed under continuous stirring for 1 hour and then filtered under vacuum. The substrates seeded with ZnO films were placed in a 100 mL screw-capped glass flask (Normax), and the solution medium for the growth of ZnO NRs was added. This glass flask containing the substrate and the solution was placed in an oven at 90 $^\circ$C for 3 h. The substrates covered with ZnO NRs were then removed from the solution, cleaned with water, ethanol and finally dried at 60 $^\circ$C.

2.3. Composite ZnO NRs/(GO, rGO) films

ZnO NRs/(GO, rGO) composite thin films were produced using the spray deposition technique (SDT). The precursor solution for SDT coating was prepared from commercial graphene oxide solution 4
mg/mL dispersed in H₂O (Sigma-Aldrich, St. Louis, USA) and Reduced graphene oxide 10 mg/mL solution stabilized with poly(sodium 4-styrenesulfonate) and dispersed in H₂O (Sigma-Aldrich, St. Louis, USA). Two different sets of samples were fabricated as follows: (a) ZnO NRs/GO composites were obtained keeping constant the deposition time and using precursor solutions for SDT with different concentrations of GO 0.1, 0.2, 0.4, and 0.8 mg/ml and (b) ZnO NRs/rGO composites were obtained keeping constant the deposition time and using precursor solutions for SDT with different concentrations of rGO 0.1, 0.2, 0.4, and 0.8 mg/ml. The rest of the parameters of deposition were the same as in the case of deposition of the seed layers.

3. Results and Discussion

SEM images of the as-synthesized pure ZnO NRs films are shown in Figure 1a. A higher magnification SEM image is shown as an inset and demonstrates that All NRs exhibited hexagonal cross-sections and generally grew almost perpendicular to the FTO surface. The average diameter of ZnO NRs is 204.2 ± 21 nm, as shown in figure 1b.

Figure 2 a-i shown SEM images of the ZnO NRs/GO and ZnO NRs/rGO composite films obtained after the spray deposition of GO or rGO nanosheets onto the surface of bare ZnO NRs. Figures 2 a-d correspond to ZnO NRs/GO composite films fabricated from precursor solution with concentrations of 0.1, 0.2, 0.4 and 0.8 mg/ml respectively and Figures 2 e-h correspond to ZnO NRs/rGO composite films fabricated from precursor solution of 0.1, 0.2, 0.4 and 0.8 mg/ml respectively. In all cases, the deposition time was maintained fixed to 8 minutes. All SEM images clearly show the presence of curled and corrugated semitransparent GO and rGO nanosheets onto the ZnO NRs. SEM images also show that using more concentrated precursor solutions results in a major coverage of the surface of the ZnO NRs films. Therefore, SEM results confirm that ZnO NRs/GO and ZnO NRs/rGO nanocomposites were successfully fabricated.
Figure 2. SEM Images of composites ZnO NRs/GO obtained from GO precursor solutions of (a) 0.1 mg/ml, (b) 0.2 mg/ml, (c) 0.4 mg/ml and (d) 0.8 mg/ml. ZnO NRs/rGO obtained from rGO precursor solutions of (a) 0.1 mg/ml, (b) 0.2 mg/ml, (c) 0.4 mg/ml and (d) 0.8 mg/ml.

Figure 3 shows the XRD patterns of (a) ZnO NRs/GO and (b) ZnO NRS/rGO composite films. All patterns have similar peaks positions which demonstrate that the presence of GO or rGO does not result in the development of new crystal orientations or changes in preferential orientations of ZnO NRs. Peaks observed at 31.7°, 34.5°, 36.3°, and 45.6° correspond to the (100), (002), (101) and (102) planes of the hexagonal ZnO wurtzite structure (JCPDS No. 36-1451). The most intense diffraction peak corresponds to the (002) plane, which indicates that the c-axis of the wurtzite structure is the preferred growth direction of the ZnO NRS. Peaks marked with (♦) are peaks corresponding to the transparent conductive substrate FTO. The characteristic peak of GO at approximately at 12°, and associated with the reflection for the (001) plane of GO, and diffraction peaks for rGO (002) diffraction peak at 26° and (1 0 0) peak at 44.5° were not observed in the XRD patterns, this is due to the low content of GO or rGO present in the composites, as well as to the strong diffractions of ZnO that could mask the peak associated to GO or rGO [17].
Figure 3. XRD patterns of (a) ZnO NRS/OG and (b) ZnO NRS/rGO composite films.

Figure 4 shows the Raman spectra of GO, rGO, ZnO NRs/GO (0.2 mg/mL), and ZnO NRs/rGO (0.4 mg/mL) composite films. Four peaks are detectable at 330, 438, 575, and 1100 cm\(^{-1}\) in the ZnO NRs Raman spectrum. The 330 cm\(^{-1}\) and 1100 cm\(^{-1}\) peaks are generated from the second-order Raman spectrum arising from zone boundary phonons of hexagonal ZnO. The intense peak that appeared at 438 cm\(^{-1}\) is assigned to the non-polar optical phonon \(E_2\) (HI) vibration mode of ZnO in the wurtzite structure \[20\]. Finally, the peak at 575 cm\(^{-1}\) corresponds to the \(E_1\) (LO) mode of hexagonal ZnO, which is associated with oxygen deficiencies \[20\]. On the other hand, the Raman spectrums of GO and rGO are dominated by two characteristic peaks of carbonaceous materials located at \(-1352\) and \(-1592\) cm\(^{-1}\), namely D and G bands, respectively \[21, 22\]. The Raman spectrum of ZnO NRs/GO and ZnO NRs/rGO composite showed similar characteristic peaks of ZnO NRs as well as G and D bands of GO.

Figure 4. Raman spectra of GO, rGO, ZnO NRs, ZnO NRs/GO and ZnONRs/rGO composites.
The photocatalytic dye degradation performances of the ZnO, ZnO/GO (0.2 mg/mL), and ZnO/rGO (0.4 mg/mL) NRs were evaluated in an aqueous solution of methyl orange (MO) dye (5ppm) under UV light irradiation, and the results are plotted in Figure 5a. The photolysis experiment showed that the MO degradation was truly driven by a photocatalytic process. The results indicate an improvement in the photocatalytic activity for both ZnO/GO and ZnO/rGO NRs compared to ZnO bare. In addition, the highest photocatalytic activity was obtained for the ZnO/rGO NRs prepared with 0.4 mg/mL concentration of rGO deposited in the surface of single ZnO NRs. 

The MO degradation process was further investigated by the first-order reaction kinetic model [23]. The rate expression is: 
\[ \ln\left(\frac{C_0}{C_t}\right) = kt \]
where \(C_0\) is the initial absorbance, \(C_t\) is the absorbance after a time \(t\), and \(k\) is the first-order rate constant. A plot between \(\ln\left(\frac{C_0}{C_t}\right)\) and reaction time is shown in Figure 5b. The estimated degradation rate constants for the ZnO, ZnO/GO (0.2 mg/mL), ZnO/rGO (0.4 mg/mL) nanorods were found to be 0.168 ± 0.003 h⁻¹, 0.440 ± 0.036 h⁻¹, and 0.845 ± 0.120 h⁻¹, respectively. It can be inferred that the photocatalytic activity of the ZnO NRs is greatly improved by the GO and rGO adhered to the ZnO surface.

The improvement of photocatalytic performance of ZnO/GO and ZnO/rGO NRs as compared to pristine ZnO NRs is must be attributed to the fact that the carbonaceous materials (rGO or GO) can act as electron transporters phases hindering the recombination of the electron-hole pair [23, 24].

**Figure 5.** (a) Photodegradation curves of methyl orange with ZnO NRs, ZnO NRs/GO, and ZnO NRs/rGO photocatalyst. (b) Kinetics plots calculated from (a) nanorods photocatalyst.

### 4. Conclusions

In summary, a series of ZnO NRs/GO and ZnO NRs/rGO composites with different concentrations of GO and rGO deposited on their surface, respectively, were fabricated. The obtained results show an effective formation of ZnO/GO and ZnO/rGO nanorods, where the adhered of GO and rGO nanosheets in the surface strongly influence the photocatalytic performance of the obtained samples. Significant enhancement of the photocatalytic efficiency of fabricated ZnO/GO and ZnO/rGO nanorods as compared with pure ZnO nanorods was determined. The enhancement in the photocatalytic activity of the ZnO/GO and ZnO/rGO nanorods is attributed to the high efficiency in light utilization and the higher transfer rate of photogenerated charge carriers from ZnO to both carbonaceous materials (rGO or GO) which inhibits the recombination processes.

### Acknowledgments

The work described in this paper was financially supported by the projects CONCYTEC (FONDECYT and GRUPO BANCO MUNDIAL) under the contract numbers N° 032-2019-FONDECYT-BM-INC.INV and N° 120-2018-FONDECYT.
References

[1] Ghowsi K, Ebrahim H R, Kazemipour-Baravati F, Bagheri H. 2014 International Journal of Electrochemical Science 9 pp 1738-1746
[2] Khataee A.R, Kasiri M.B. 2010 Journal of Molecular Catalysis A: Chemical 328 pp 8-26
[3] Singh P, Borthakur A. 2018 Journal of Cleaner Production 196 pp 1669-1680
[4] Yagub M T, Sen T K, Afroze S, Ang H.M. 2014 Advances in Colloid and Interface Science 209 pp 172-184
[5] Gadekar M R, Ahammed M.M. 2016 Desalination and Water Treatment 57 pp 26392-26400
[6] Bilinska L, Gmurek M. 2021 Water Resources and Industry 26 100160
[7] Giwa A, Yusuf A, Balogun H A, Sambudi N S, Bilad M R, Adeyemi I, Chakraborty S, Curcio S. 2021 Process Safety and Environmental Protection 146 pp 220-256
[8] Ahmed S N, Haider W. 2018 Nanotechnology 29 342001
[9] Opoku F, Govender K K, van Sittert C G C E, Govender P P. 2017 Advanced Sustainable Systems 1 1700006
[10] Zhu D, Zhou Q. 2019 Environmental Nanotechnology, Monitoring & Management 12 100255
[11] Lee K M, Lai C W, Ngai K S, Juan J C. 2016 Water Research 88 pp 428-448
[12] Zhang Y, Mandal R, Ratchford D C, Anthony R, Yeom J. 2020 Nanomaterials 10 491
[13] Qi K, Cheng B, Yu J, Ho W. 2017 Journal of Alloys and Compounds 727 pp 792-820
[14] Raizada P, Sudhaik A, Singh P. 2019 Materials Science for Energy Technologies 2 pp 509-525
[15] Abebe B, Ananda Murthy H.C, Amare E. 2020 Environmental Nanotechnology, Monitoring & Management 14 100336
[16] Rokshat E, Akhavan O. 2016 Applied Surface Science 371 pp 590-595
[17] Ramos P G, Luyo C, Sánchez L A, Gomez E D, Rodriguez J M. 2020 Catalysts 10 660
[18] Ravichandran K, Uma R, Sriram S, Balamurgan D. 2017 Ceramics International 43 pp. 10041-10051
[19] Rodriguez J, Feuillet G, Donatini F, Onna D, Sanchez L, Candal R, Marchi M C, Bilmes S A, Chandezon F. 2015 Materials Chemistry and Physics 141 pp. 378-384
[20] Mwankemwa B S, Nambala F J, Kyeyune F, Hlatshwayo T T, Nel J M, Diale M. 2017 Materials Science in Semiconductor Processing 71 pp. 209-216
[21] Kumar P, Som S, Pandey M K, Das S, Chanda A, Singh J. 2018 Journal of Alloys and Compounds 744 pp. 64-74.
[22] S. Prabhu, M. Pudukudy, S. Sohila, S. Harish, M. Navaneethan, D. Navaneethan, R. Ramesh, Y. Hayakawa, Optical Materials 79 (2018) 186-195
[23] Ramos P G, Flores E, Luyo C, Sánchez L A, Rodriguez J. 2019 Materials Today Communications 19 pp. 407-412
[24] Jiang H, Zhang X, Gu W, Feng X, Zhang L, Weng Y. 2018 Chemical Physics Letters 711 pp. 100-106