



Original Article

Facile Hydrothermal Method for Fabrication of Seedless ZnO Nanorod/GO Composite on PCB

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Abstract: Herein we report on a simple method to grow ZnO nanorod/Graphene oxide (GO) array without the initial seed layer on a printed circuit board (PCB) as the substrate based on Galvanic effect. The hydrothermal growing conditions such as temperature and time were investigated by X-ray diffractometry (XRD), Raman scattering, as well as Scanning Electron Microscopy (SEM). It is shown that the as-prepared ZnO nanorod was grown well-vertically on the substrate. Furthermore, we investigated the photocatalytic activity of synthesized samples, which showed the enhanced photodegradation ability in the composite sample.

Keywords: Seedless, ZnO array, hydrothermal, ZnO/GO composite

1. Introduction

ZnO is one of the most studied oxide semiconductors because of its prominent characteristics such as wide direct bandgap (~3.37 eV), large exciton binding energy (60 meV) at room temperature, environmental friendliness, and low-cost [1-3]. Hence many works have focused on the fabrication with various wet-chemical methods which mainly produced ZnO in the powder form. There were several

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works that tried to prepare it on substrates in order to have well-aligned ZnO nanorod array seeking interesting applications in electronics and microdevices [4]. However growing ZnO on substrate, one usually has to have a precious substrate with ZnO seed initially, which may drastically increase the production cost. Furthermore, the low stability of the seed on the substrate due to different thermal expansion and crystal lattice characteristics between ZnO and the substrate is the main reason for this fabrication technique far from applicable [5-7].

Herein we proposed an ecofriendly hydrothermal technique to fabricate well-aligned ZnO array on a printed circuit board (PCB) substrate thanks to Galvanic effect. We also prepared the composite of ZnO and graphene oxide (GO) for further study of the photocatalytic activity in degradation of methylene blue in solution. The crystal structure and morphological properties of synthesized samples were characterized by X-ray diffractometry (XRD), Raman spectroscopy, and Scanning Electron Microscopy (SEM).

2. Experimental

2.1. Chemicals and Synthesis of Materials

Based on Galvanic effect, ZnO nanorod array was grown on printed circuit board – PCB by a hydrothermal method [8]. First, the PCB substrate was polished with SiC sandpaper. Then the PCB substrate was ultrasonic cleaned with acetone, ethanol and bi-distilled water. In order to make the structure of Galvanic cell, the edges of PCB substrate were covered by Sn metal. The uncoated area would develop ZnO nanorods as schematically shown in Figure 1.

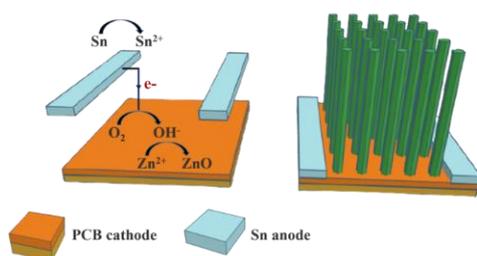


Figure 1. Schematic illustration of Galvanic cell-based fabrication process of ZnO nanorod arrays. Sn was used as the sacrificing anode and ZnO nanorod would grow on the cathode substrate.

To prepare ZnO array, the prepared Galvanic cell substrate was immersed in a mixture of 100 mM zinc nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$); to prepare ZnO/GO composite, modified Hummer's method graphene oxide (GO) [9] was poured in the above solution. Then, the resulted solution was magnetically stirred in 15 min and consequently placed in a Teflon thermos flask covered by a stainless steel for the hydrothermal process at 90°C in 10 hours. After that, substrate was rinsed with distilled water to remove residual salts from the surface. Finally, the sample was air-dried naturally. The preparation process was schematically shown in Figure 2.

2.2. Characterization

The crystal structure of the ZnO nanorods was characterized by X-ray diffraction and Raman spectroscopy. The morphology of the sample surface was examined by scanning electron microscopy (SEM). While the absorbance spectra of the dye was analyzed at regular intervals of time by UV-Vis spectrophotometer.

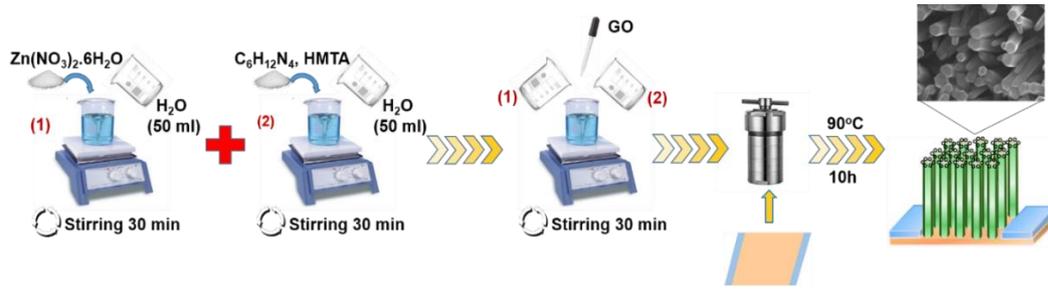


Figure 2. Preparation process for ZnO and ZnO/GO nanorod arrays.

2.3. Photocatalytic Activity Measurement

The degradation of methylene blue dye in the solution under sunlight irradiation was used to evaluate the photocatalytic activity of the synthesized samples. MB solution with $C = 25 \times 10^{-6} \text{ mol.L}^{-1}$ and the ZnO nanorod arrays were used in the measurement. The material was added to 150 ml of MB solution. Then, we began measuring the photocatalytic ability of the material under direct sunlight irradiation. The degradation of MB was measured after every 1 hr of sunlight irradiation for a total time of 10 hr by using a UV-Vis system. The MB degradation efficiency can be calculated as [10]:

$$\eta(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

where C_0 is the MB initial absorption value and C_t is the MB absorption value at the time of irradiation t .

3. Results and Discussion

3.1. Structural Property

Figure 3 shows XRD patterns of ZnO and ZnO doped 0.5 ml GO samples. The 2θ -peaks of these samples appear at 32.07° , 34.73° and 36.54° corresponding to planes of (100), (002), and (101), respectively. These planes match with the characteristic hexagonal wurtzite crystal structure of ZnO (JCPDS card No. 36-1451) [10]. Both the XRD patterns show no other peaks of impurity or any other forms of ZnO such as $\text{Zn}(\text{OH})_2$ so ZnO and ZnO/GO samples that have a high purity.

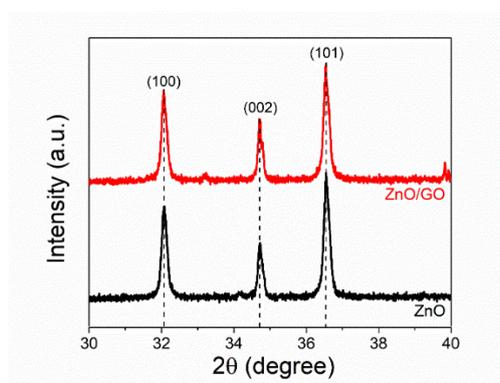


Figure 3. XRD patterns of ZnO and ZnO/GO nanocomposite.

To study the binding medium and the defect-related disorder in the mixture of ZnO and GO-ZnO, Raman analysis was performed. Raman spectra of ZnO and ZnO/GO are presented in Figure 6. The spectrum of ZnO shows the peak at 332 cm^{-1} corresponding to zone boundary phonons of hexagonal ZnO. The peaks at 438 cm^{-1} and 575 cm^{-1} which belong to characteristic E_2 mode (High) and A_1 mode (LO) of wurtzite type phase of ZnO [13], [14]. In addition to the two characteristic vertices of the wurtzite hexagonal phase of ZnO, the Raman spectra of ZnO/GO show two major characteristic peaks at ~ 1350 and 1580 cm^{-1} corresponding to D band and G band of GO, respectively [15, 16]. The D band appears due to sp^3 disabilities while G band is due to in plane oscillation of sp^2 carbon atoms and a doubly degenerated phonon mode [13], [17]. Due to GO doping, the intensity of the E_2 mode (high) peak is slightly decreased.

3.3. Morphological Analysis

Figure 5 shows the SEM image of ZnO nanorod array being air-dried. It confirms the one-dimensional hexagonal morphology of ZnO. High density ZnO nanorods, which grow upright and bond well with the PCB substrate. That also means that the fabrication of ZnO nanorod arrays on the PCB substrate by the seedless hydrothermal method has been successful.

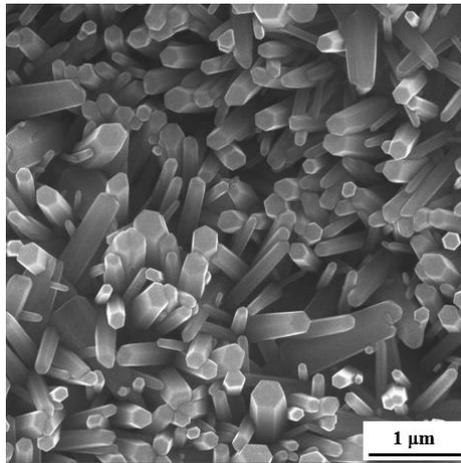


Figure 5. SEM image of ZnO nanorod arrays being air-dried.

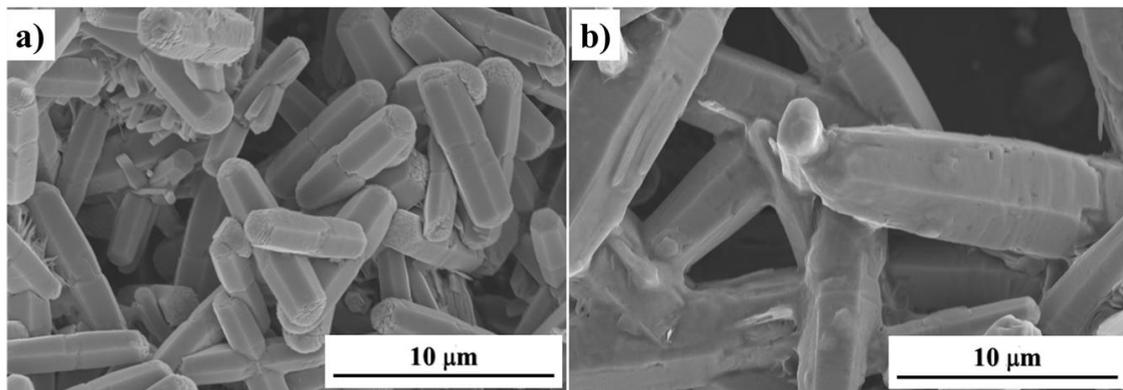
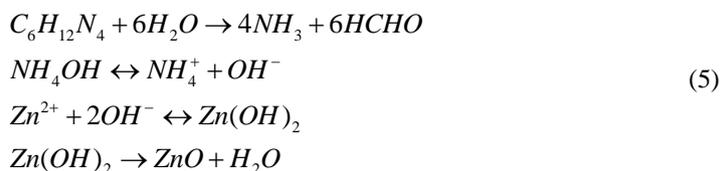


Figure 6. SEM image of: (a) ZnO and (b) ZnO/GO nanorod arrays being dried at 100°C .

However, during the photocatalytic investigation, when immersed in the solution, the material is unstable, and peeled off from the base. To enhance durability and reusability, the material is dried at 100°C and an SEM image is obtained as shown in Figure 6a. The morphology of the material has changed significantly. The nanorods were morphologically uniform but in random directions. After deposition of GO layer on the surface of ZnO nanorods, the hexagonal morphology is preserved. However, the size of the nanorods in the case of ZnO/GO nanocomposites was slightly smaller than that of ZnO nanorods (Table 1). The coating of GO on ZnO enables photo-electrons to easily transfer from the ZnO surface to the GO layers, leading to separation of the photogenerated carriers and improving the photocatalytic efficiency of the nanocomposite [12].

These observations demonstrate that ZnO nanorods can be grown directly on PCB substrates by hydrothermal method based on Galvanic cell structure with high ZnO nanorod density without prepared seed layers. Accordingly, precursor mixtures of $Zn(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}N_4$ was the nuclei source for the growth of ZnO, of which $Zn(NO_3)_2$ provided Zn^{2+} and $C_6H_{12}N_4$ hydrolyzed to produce formaldehyde and ammonia. Ammonia reacts with water to form NH_4OH , dissociates rapidly into OH^- and NH_4^+ . $C_6H_{12}N_4$ acts as a pH buffer to adjust the pH value of the solution and remains constant at 7.0. The OH^- ions react with Zn^{2+} to form $Zn(OH)_2$ compounds that then decompose to ZnO [8].



Galvanic effects are formed by exposing two different metals to each other. Here, the PCB substrate already has a copper layer on the surface, so it is preferred to choose metals with stronger reducing properties than Cu such as Al, Pb, Sn ... to cover the edges of the substrate. Because of the more negative reduction potential of Sn in comparison with Cu, Sn loses electrons to form Sn^{2+} , and the lost electrons are transferred to the PCB substrate. Therefore, the Sn layer acted as the sacrificing anode and the PCB substrate acted as the cathode. As a result, by coating the edges of the PCB substrate with the Sn layer, the potential difference of the two electrodes is produced. The difference in potentials (potential differences) promotes chemical reactions, so they induce growth of ZnO on the exposed substrate area [18].

3.4. Photocatalytic Study

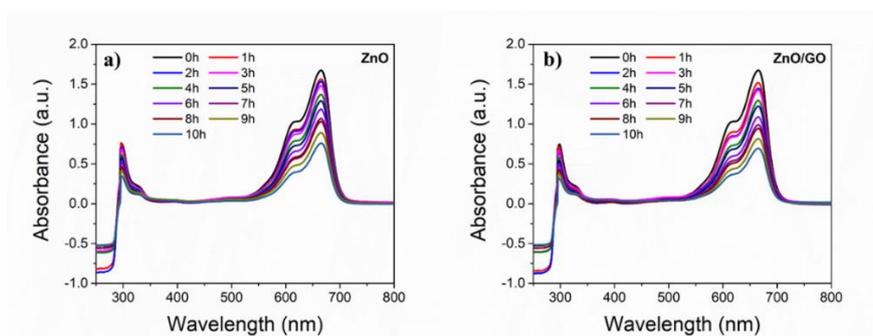


Figure 7. UV-vis absorbance spectra of MB dye under sunlight after different time intervals using (a) ZnO and (b) ZnO/GO nanocomposite as catalysts.

The ZnO and ZnO/GO nanocomposites were used as photocatalyst for decolorization of MB dye utilizing sunlight as an energy source. UV–vis absorbance spectrum of the dye solution gives characteristic MB dye peaks with absorbance intensity directly proportional to its concentration (according to Beer-Lambert law). Figures 7a and b show that the absorbance intensity of dye decreases with respect to sunlight irradiation time using ZnO and ZnO/GO nanocomposites as catalyst. The decoloration of MB dye is attributed to the oxidation of the dye in the presence of hydroxyl radicals. After 10 hours of irradiation, the photocatalytic efficiency of the pure ZnO sample was about 54.65% while GO doped ZnO sample was increased up to 58.53%. It was shown that GO doping into ZnO nanorods increased the efficiency of the photocatalytic reaction to treat MB dyes in sunlight irradiation.

The study of the process of doping GO into ZnO materials to increase the photocatalytic efficiency stems from the following reasons. First, the surface area of graphene is high so the appearance of GO can increase the absorption of the composite. On the other hand, the absorption of the photocatalytic agent is further enhanced by π - π conjugation between the aromatic regions of GO and MB. Secondly, under UV irradiation, electrons of the valence band (VB) are excited to jump onto the conduction band of ZnO through the GO sheets and then captured by O_2 to generate and O_2^- . At the same time, the emitted electrons from the conduction band of ZnO can be switched to GO, which greatly contributes to the resistance of charge recombination, helping to prolong the life of electrons and holes [19].

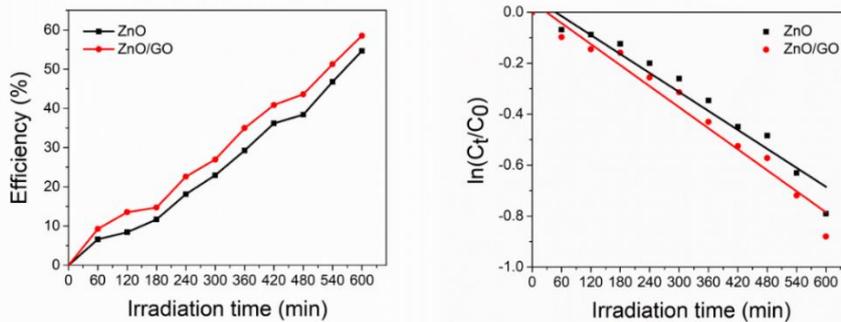


Figure 8. a) Photocatalytic ability of synthesized samples for MB degradation, b) The first-order kinetics for MB degradation with irradiation time.

For further understanding the photocatalytic process of GO doped ZnO sample, a rate kinetic study was carried out by using two models: first-order and second-order models. The rate kinetics of the photocatalytic process of the synthesized samples was suitable for the first-order model as shown in Figure 8b, where their kinetic constants could be expressed as follows:

$$k = \frac{1}{t} \ln \frac{C_0}{C_t} \quad (6)$$

where C_0 and C_t are the initial concentration of MB and the concentration of MB at time t , the irradiation time, respectively. The fitted k values and their correlation parameters shown in Table 2 indicate that the degradation rate constant for ZnO/GO is higher than that of the ZnO. It shows that higher dye decolorization rate can be achieved by the addition of GO to ZnO nanomaterial.

Table 2. The first-order rate constants of synthesized samples.

Sample	Reaction rate constant k (min^{-1})	R^2
ZnO	0.0012	0.95071
ZnO/GO	0.0013	0.96513

3.5. Photocatalytic Activity Mechanism

ZnO semiconductor has a rather large band gap (3.37 eV) while light has a long wavelength, so it is difficult for electrons to transfer energy levels. To increase the photocatalytic capacity it is usually to create defects by doping or fabrication. Graphene oxide has many advantages, which are very suitable for ZnO doping selection. When the ZnO / GO nanocomposite is exposed to sunlight, the photo-excitation of electrons (e-) on the surface of the ZnO takes place. When photons with energies greater than the band gap energy of the photocatalyst are absorbed, electrons of the valence band (VB) are excited to the conduction band (CB) of the ZnO via the GO sheet, leaving positive holes in VB. It facilitates some photochemical reactions to take place. The GO lower work function allows for efficient electronic interaction between GO and ZnO, so that electrons are easily transferred from the CB of ZnO to GO. This helps prolong the recombination time of the electron-hole pair (e⁻ – h⁺ pair) . The electrons in CB react with surface oxygen species and water molecules to produce reductive superoxide radicals (O₂^{•-}) and oxidative hydroxyl radicals (•OH / •OOH) while the positive holes in VB can oxidize organic pollutants directly or produce highly reactive hydroxyl radicals (•OH).These hydroxyl radicals (•OH) are highly reactive oxidizing agents and rapidly decompose dyes into less detrimental products. The possible reactions during dye decolorization MB are summarized in Eqs. (6) - (14) and shown in a schematic form in Figure 9 [13].

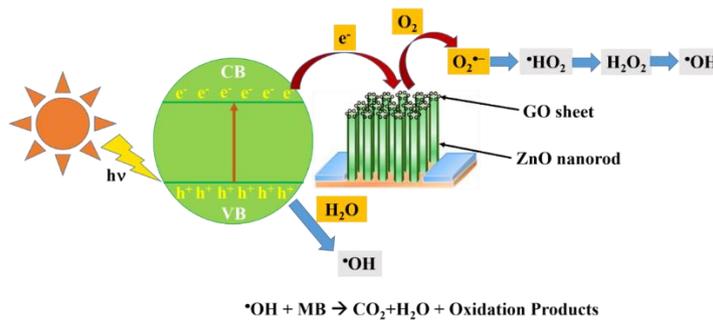
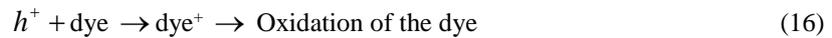
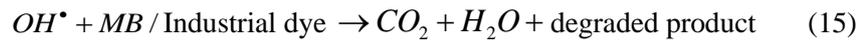


Figure 9. Schematic show of the reduction mechanism of MB dye by using the ZnO/GO nanocomposite as a photocatalyst under sunlight.

4. Conclusion

This work reported on a facile seedless hydrothermal synthesis of ZnO nanorod array on PCB substrate using Galvanic effect. It showed that ZnO array was grown vertically on the substrate. Furthermore, ZnO/GO composite fabricated using this technique showed the enhancement of photocatalytic activity. This method could be useful for cost-effective nanorod ZnO array fabrication.

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References

- [1] T. Bora, P. Sathe, K. Laxman, S. Dobretsov, J. Dutta, Defect Engineered Visible Light Active ZnO Nanorods for Photocatalytic Treatment of Water, *Catalysis Today*, Vol. 284, 2017, pp. 11-18 <https://doi.org/10.1016/j.cattod.2016.09.014>.
- [2] P. R. Chithira, T. T. John, The Influence of Vacuum and Annealing on the Visible Luminescence in ZnO Nanoparticles, *Journal of Luminescence*, Vol.185, 2017, pp. 212-218 <https://doi.org/10.1016/j.jlumin.2017.01.022>.
- [3] M. Kahouli, A. Barhoumi, A. Bouzid, A. Al-Hajry, S. Guerhazi, Structural and Optical Properties of ZnO Nanoparticles Prepared by Direct Precipitation Method, *Superlattices and Microstructures*, Vol. 85, 2015, pp. 7-23 <https://doi.org/10.1016/j.spmi.2015.05.007>.
- [4] J. Miao, B. Liu, II-VI Semiconductor Nanowires, *Series in Electronic and Optical Materials*, Woodhead Publishing, Amsterdam, 2015, pp. 3-28 <https://doi.org/10.1016/b978-1-78242-253-2.00001-3>
- [5] M. T. Man, J. -H. Kim, M. S. Jeong, A. -T. T. Do, H. S. Lee, Oriented ZnO Nanostructures and Their Application in Photocatalysis, *Journal of Luminescence*, Vol. 185, 2017, pp. 17-22 <https://doi.org/10.1016/j.jlumin.2016.12.046>.
- [6] Y. Zhang, M. K. Ram, E. K. Stefanakos, D. Y. Goswami, Synthesis, Characterization, and Applications of ZnO Nanowires, *Journal of Nanomaterials*, Vol. 2012, 2012, pp. 1-22 <https://doi.org/10.1155/2012/624520>.
- [7] R. Lv, X. Wang, W. Lv, Y. Xu, Y. Ge, H. He, G. Li, X. Wu, X. Li, Q. Li, Facile synthesis of ZnO nanorods grown on graphene sheets and its enhanced photocatalytic efficiency, *Journal of Chemical Technology & Biotechnology*, 90 (2015) 550-558 <https://doi.org/10.1002/jctb.4347>.
- [8] H. H. Mai, D. H. Tran, E. Janssens, Non-enzymatic Fluorescent Glucose Sensor Using Vertically Aligned ZnO Nanotubes Grown by a One-step, Seedless Hydrothermal Method, *Mikrochim Acta*, Vol. 186, 2019, pp. 245 <https://doi.org/10.1007/s00604-019-3353-5>.
- [9] T. D. Phan, C. M. Vo, T. M. T. Tran, T. L. A. Luu, X. S. Nguyen, Structural and Bandgap Properties of Titanium Dioxide Nanotube/graphene Oxide Composites Prepared by a Facile Hydrothermal Method, *Materials Research Express*, 6 (2019) 105054 <https://doi.org/10.1088/2053-1591/ab3a0b>.
- [10] A. S. Mohammad, I. Uddin, D. -T. Phan, G. -S. Chung, Synthesis of ZnO Nanoparticles-reduced Graphene Oxide Composites and Their Intrinsic Gas Sensing Properties, *Surface Review and Letters*, Vol. 21, 2014, pp. 1450086. <https://doi.org/10.1142/s0218625x14500863>.
- [11] X. -S. Nguyen, M. -Q. Nguyen, X. -T. Trinh, A. C. Joita, S. V. Nistor, Correlation of Native Point Defects and Photocatalytic Activity of Annealed ZnO Nanoparticle Studied by Electron Spin Resonance and Photoluminescence Emission, *Semiconductor Science and Technology*, Vol. 35, 2020, pp. 095035. <https://doi.org/10.1088/1361-6641/aba168>.
- [12] I. Boukhoubza, M. Khenfouch, M. Achehboune, L. Leontie, A. Carlescu, C. Doroftei, B.M. Mothudi, I. Zorkani, A. Jorio, Graphene Oxide Coated Flower-shaped ZnO Nanorods: Optoelectronic Properties, *Journal of Alloys and Compounds*, Vol. 831, 2020, pp. 154874. <https://doi.org/10.1016/j.jallcom.2020.154874>.

- [13] P.S. Chauhan, R. Kant, A. Rai, A. Gupta, S. Bhattacharya, Facile Synthesis of ZnO/GO Nanoflowers over Si Substrate for Improved Photocatalytic Decolorization of MB Dye and Industrial Wastewater under Solar Irradiation, *Materials Science in Semiconductor Processing*, Vol. 89, No. 2019, pp. 6-17 <https://doi.org/10.1016/j.mssp.2018.08.022>.
- [14] M. Šćepanović, M. Grujić-Brojčin, K. Vojisavljević, S. Bernik, T. Srećković, Raman Study of Structural Disorder in ZnO Nanopowders, *Journal of Raman Spectroscopy*, Vol. 41, 2010, pp. 914-921 <https://doi.org/10.1002/jrs.2546>.
- [15] S. X. Nguyen, T. T. Tung, P. T. L. Huong, N. H. Tho, D. Losic, Heterojunction of Graphene and Titanium Dioxide Nanotube Composites for Enhancing Photocatalytic Activity, *Journal of Physics D: Applied Physics*, Vol. 51, 2018, pp. 265304. <https://doi.org/10.1088/1361-6463/aac7ce>.
- [16] P. V. Tuan, T. T. Phuong, V.T. Tan, S. X. Nguyen, T. N. Khiem, In-situ Hydrothermal Fabrication and Photocatalytic Behavior of ZnO/reduced Graphene Oxide Nanocomposites with Varying Graphene Oxide Concentrations, *Materials Science in Semiconductor Processing*, Vol. 115, 2020, pp. 105114 <https://doi.org/10.1016/j.mssp.2020.105114>.
- [17] S. Alamdari, M.S. Ghamsari, H. Afarideh, A. Mohammadi, S. Geranmayeh, M. J. Tafreshi, M. H. Ehsani, M. H. Majles ara, Preparation and Characterization of GO-ZnO Nanocomposite for UV Detection Application, *Optical Materials*, Vol. 92, 2019, pp. 243-250. <https://doi.org/10.1016/j.optmat.2019.04.041>.
- [18] H. C. Hieu, P. V. Thanh, N. V. Tuyen, M. H. Hanh, A Simple, One-step, Seedless Hydrothermal Growth of ZnO Nanorods on Printed Circuit Board Substrate, *VNU Journal of Science: Mathematics - Physics*, Vol. 33, 2017, pp. 29-33 <https://doi.org/10.25073/2588-1124/vnumap.4200>.
- [19] S. Xu, L. Fu, T. S. H. Pham, A. Yu, F. Han, L. Chen, Preparation of ZnO Flower/reduced Graphene Oxide Composite with Enhanced Photocatalytic Performance under Sunlight, *Ceramics International*, Vol. 41, 2015, pp. 4007-4013 <https://doi.org/10.1016/j.ceramint.2014.11.086>.