Plant Archives Vol. 20, Supplement 2, 2020 pp. 1005-1008 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

NOVEL AND LOW-COST SYNTHESIS OF ZNO NANOROD COATED BY GRAPHENE OXIDE FOR ENHANCED PHYSICAL ABSORPTION OF ZNR FROM UV TO VIS-IR REGION

Lina Z. Yahiya*, Mohamed K. Dhahir and Rawaa A. Faris
Institute of laser for postgraduate Studies, University of Baghdad, Baghdad, Iraq

Abstract

Enhanced activity of ZnO nanorod (ZNR) absorption have been synthesized a graphene coated nano rod (ZNR@Gr) via electrostatic self-assembly methods. The morphologies of ZNR@Gr and ZNR have been studied by (FE-SEM), (TEM, HR-TEM), and (AFM), which refers to graphene oxide was coated ZNR with five layers (ZNR@Gr). The optical properties can be represented by UV-Vis absorption spectra. As a result, all samples with high absorption at UV region of spectrum then Increased the absorption when coated the ZNR by GO at (387–1000) red shift accrues when the energy band gap decreases from (3.2 to 2.7) eV. ZNR and ZNR@Gr have been synthesized by simple method, cheap and environmentally, which made it favorable for huge -scale preparation in many applications as water splitting, sensor, Soler cell and optoelectronic devices.
***Keywords*:** ZnO nanorod, graphene oxide, absorption, synthesis, Band gup, coated

Introduction

Because of ZnO nanorod is high photosensitivity and stability semiconductor, it has attracted interest as one of the important photocatalysts. (Elnaz Mohammedi *el al.,* 2017) ZnO has wide band gap 3.37 eV therefore, the photocatalytic efficiency remains very low (Mundher. A. Hassan *et al.,* 2012) that Due to, limit of emission efficiency of ZnO nanorods at ultraviolet (UV) region and its application in light emission diodes LEDs. (Naganori Dougami *et al.,* 2003); (Yenning Yang *et al.,* 2015) because of the exhalent physical properties of graphene, Huge studies were enhanced the bandgap emission on ZnO by coated with graphene. (Chih Wei Lai *et al.,* 2005); (You, *et al.,* 2007); (Abiyasa, *et al.,* 2007); (Chen *et al.,* 2008); (Cheng *et al.,* 2008). It is become a rising star in material science application in optoelectronic devices, nanocomposites, sensors and solar cells. (Omid Akhavan *et al.,* 2010); (Fana Yuanjun *et al*., 2017) Graphene has large surface area and high thermal conductivity, high absorption in IR regain of light spectra there for, it was a novel material for energy storage applications. (Xuan Wang *el al.,* 2008); (Yanping Zhang *el al.,* 2009) graphene oxide (GO) has ability of water dispersion make it as hydrophilic material that means to write graphene oxide (GO), is easily to synthesize for a coated of ZNR. (Schedin *el al.,* 2008) The photocatalytic performance of ZnO was improved by combining with graphene, or carbon network. (Ferrari *el al.,* 2015) Because of its abundant surface chemical functional groups (oxygen epoxide groups, hydroxyl groups, carboxyl groups, etc.), the covalent bonding of hydrogen become available to the graphene-based composite (Satyendra Mishra *el al.,* 2018). Despite of a great type of ZnO graphene composites was been reported, only few reports on ZNR coated with graphene. In this paper, we synthesized ZnO nanorod (ZNR) coated by graphene oxide (ZNR@Gr) by simple method and low cost then tested by the SEM, TEM, HRTEM and AFM images shows that graphene with 5 layers were plated on the surface of ZNR and the optical properties was studied by UV-Vis absorption spectra to improve the absorption of ZnO nano rod from UV range to VIS-IR region of light spectra.

Materials and Methods

Experimental

The ZNR were synthesis in two steps. Step one of the FTO substrates were washed with 50 ml of water, 25 ml of ethanol, and 25ml acetone in an ultrasonic bath for 20 min at 90 ºC. Then, 10 drops of hexamethylenetetramine (HMTA, 0.5 M) from New Delhi-110002 (INDIA) and 10 drops of Zn $(NO_3)^2$ solution from (Shanghai, China), (0.5 M) were alternately distilled onto the FTO (fluorine-doped tin oxide) substrate. After interacting for 10 min, the solution on (FTO, 2× 3 cm^2) substrates was removed by using a spinner then, the FTO was annealed at 200 ºC for 20 min. To be sure that the seeds are formed on the substrate all above process should be repeated for 3 times by using hydrothermal method. Samples of ZnO nano seeds substrates were prepared with were stood up right into stainless-steel autoclave at 122 ºC for 4h then two days at room temperature including the mixed solution of 0.05 M HMTA and 0.05 M Zn $(NO_3)^2$. Then, all the samples were cleaned by deionized water and desiccate at 100 ºC for 4 h.

Graphene oxide Preparation

To production graphene oxide (GO) was used Hummers method (Schedin *el al.,* 2008). In summary, 1 g of graphite powder with partial size (6-8 nm) from (sky spring nanomaterials, west hollow Drive. Houston, TX.77082.USA) was added to 23ml of H_2SO_4 98% (LOBA -Chemise) with 5g of sodium nitrate $NaNO_3$ solution was washed by 5%M of HCl (11.25) +H_2O (88.75) 37.5% (Fluke). finally, to obtain GO the solution was heated at 100 C° for 3 h.

Synthesis ZNR coated by graphene (ZNR@Gr)

- By an electrostatic self-assembly method the ZNR arrays were coated with graphene.
- The ZNR surface was modified with APTMS aminopropyltrimethoxysilane was bought from Aladdin (Shanghai, China), in 5% APTMS/ethanol solution obtained a positively charged surface. Then, 5 mL 0.1 mg mL^{-1} negatively charged.

- centrifuged at 9000 rpm for 25 min, it was increased to 100 mL and ultrasonically for 20 min.
- The modified substrates could submerge in GO solution with heating at 65 ℃ for 4 h.
- The products were cleaned with deionized water and desiccate at 60 ℃ (ZNR@GO).
- ZNR & GO could anneal at 500 ℃ for 1 hour to obtain ZNR@Gr nanorod as Fig. 1.

Results and Discussion

Characterization of ZNR and ZNR@Gr

Fig 2 (a) shows the AFM (Atomic force microscopy AFM JPK nano wizard Germany) Image of ZNR, it can be seen that of image (a), are uniform and homogenies, which appeared better nucleation centers for the formation of well arrangement compared with another image b. of ZNR@Gr, was uniform with average range size distribution less than 90 nm with roughness average (22,6) nm while, the distribution average of size of ZNR less than 10.05 nm and with roughness average (3.5nm). GO the distribution average size was not more than 250 nm, which corresponds was very good of ZNR to form the ZNR@Gr structure as shows in Fig. 2, b thickness of most GO is about 2.63 nm (agree with Yuzhi Zhang *et al.,* (2019), which corresponds to 5 layers of GO. The (EDX) given in Fig.3 (a) showed the presence of (Zn, O) and Si, comes from substrate) with high intensity of (Zn. Fig 3 b) (Zn O, C) and Si from substrate when coated ZNR by GO.

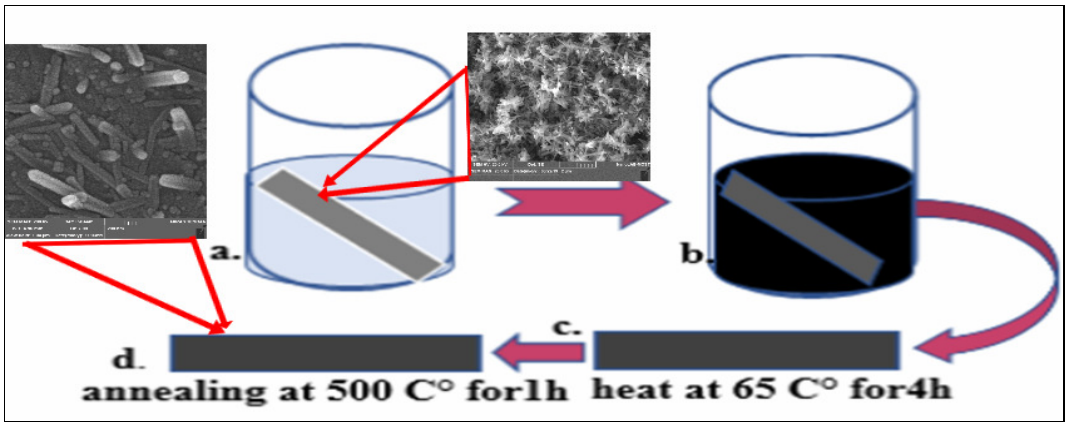

Fig. 1 : The stapes of ZNR coated with graphene (ZNR@Gr) a. APTMS/ethanol solution a. appositively charges solution b. graphene oxide (GO) negatively charge solution c. FTO substrate with ZNR@GO thin film. d. FTO substrate with ZNR@Gr thin film.

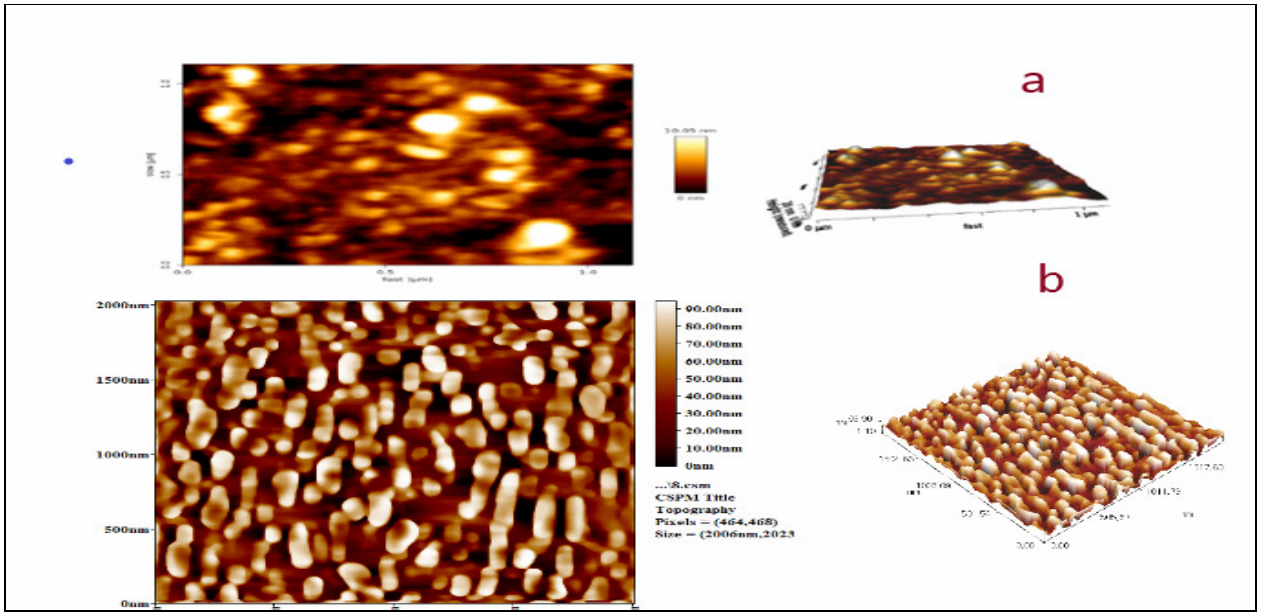

Fig. 2 : An atomic force microscopy AFM of ZNR., b. AFM of ZNR@Gr

Fig 4 a. refers to (ZNR) that grow larger length, high density rod to rod separation and a random arrangement or horizontally growth. The typical TEM images of ZNR@Gr were shown in Fig. 4 (b. c) It was specified from the image in low enlargement Fig. 4(b, c) that the zinc oxide nanorods are randomly distributed on ZNR@Gr. The ZnO nanorods were noted very visibly from the high magnification images (Fig. 4c). we can observe the wrinkles on the ZNR surface at fig 4 (b,c) when graphene connecting the ZNR arrays . The graphene was observed in the SEM (FE-SEM, MIRA3 TESCAN, Meshhed) image is already relatively thick at Fig. 4(d, e). It can be seen in the TEM and HTEM (HRTEM, Tecnai G2 F20, FEI Company, USA), images of the surface of ZNR was good coated by graphene uniformly, which was not more than 5 layers thick at Fig. 4 (b,c,f) (agree with Yuzhi Zhang *et al.* , (2019)).

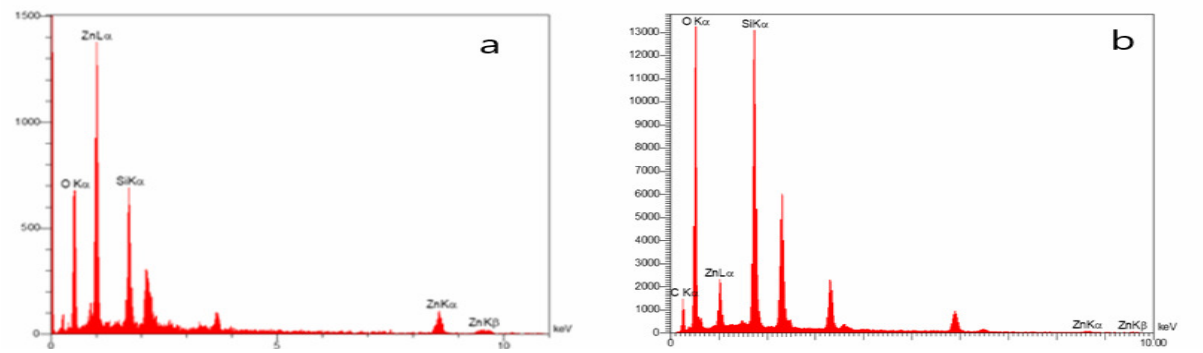

Fig. 3a,b : (EDX)for, ZNRand ZNR@Gr

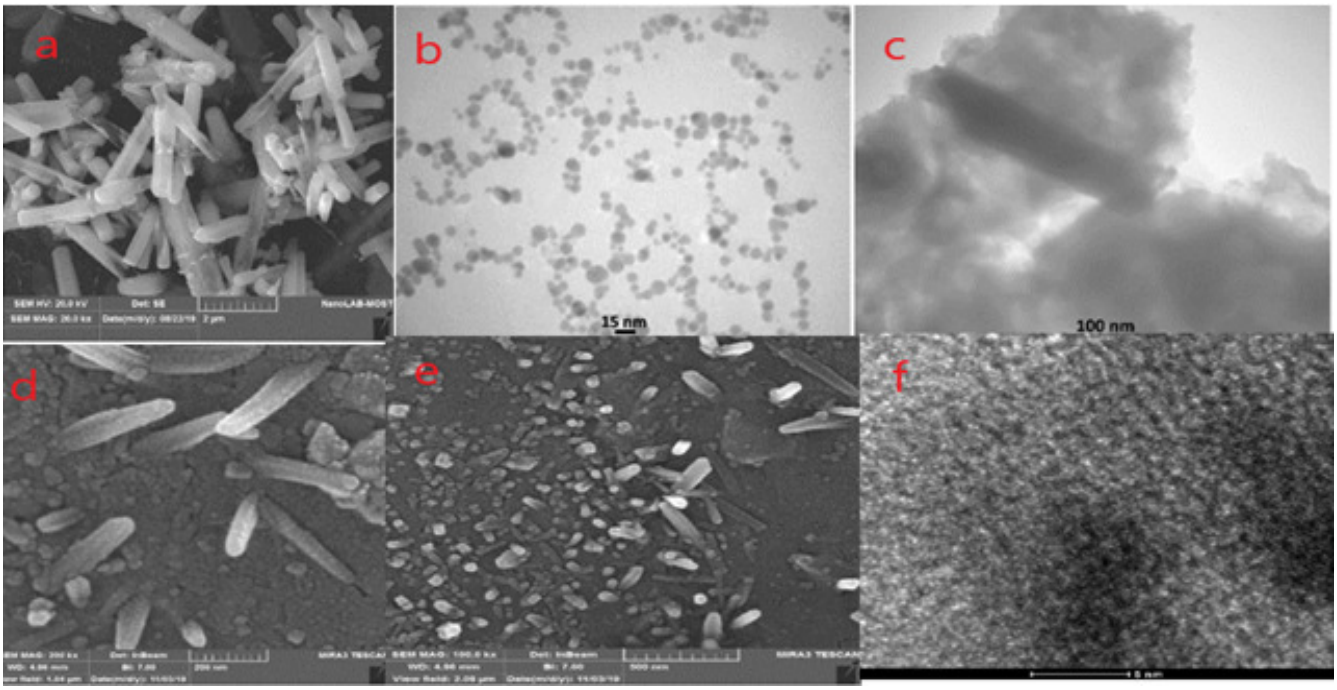

Fig. 4 : a (FE-SEM) image of ZNR, b,c.TEM image of ZNR@Gr. d, e. FE-SEM image of ZNR@Gr and HRTEM image f, for ZNR@Gr.

3.2 Optical properties Characterization of ZNR@Gr

The UV-Vis absorption (SP8001 Taiwan) of ZNR, ZNR@Gr, could obtain with the wavelength ranges of 350–1000 nm and 350–700 nm. The UV- VIS spectra (Fig. 5(a)) exhibit that for all samples, with a high absorption in the ultraviolet region and Increase in the light intensity of absorption in the range of 387–1000 nm red shift occurs when coated ZNR by graphene oxide. (agree with Yuzhi Zhang *et al.* (2019)) The optical band gaps of the thin film were obtained when $(\alpha h\nu)^2$ is plotted against photon energy (hv) at Fig. 5(b) straight line, which mention that the absorption edge is lead to a direct transition between valence and conduction bands. The intercept of the straight line on hv axis matches to the optical band gap (Eg). The band gap was degreased at the ZNR 3.2 eV and 2.7 eV of ZNR@Gr. The energy band gap decreases as particle size of the semiconductor nanomaterials increased (agree with Madan Singh *et al.* (2018).

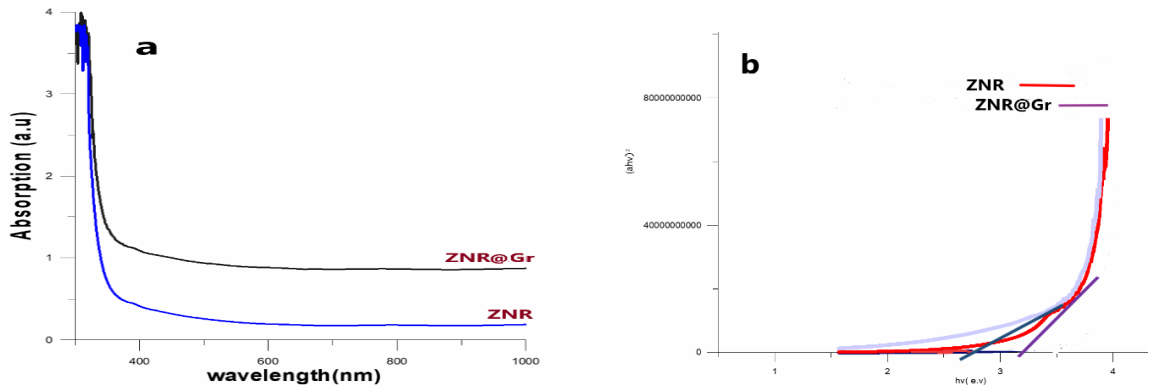

Fig. 5 : (a) UV-visible spectra of ZNR, ZNR@Gr (b)direct optical energy plotted for sample ZNR and ZNR@Gr

Conclusions

The solution reduction and electrostatic self-assembly could develop preparation ZNR@Gr. The SEM and TEM, HTEM images indicated that ZNR was covered with 5 layers of graphene lead to reused in energy band gap and increased in optical absorption. The low cost of composite material was display to improve light absorption and that was very useful for may photonic application.

Acknowledgments

This work was supported by Dr. Zainab F. Mahdi at the Institute of Laser for postgraduate studies, University of Baghdad.

References

Abiyasa, A.P.; Yu, S.F.; Lau, S.P.; Leong, E.S.P. and Yang, H.Y. (2007). Enhancement of ultraviolet lasing from Accumulated highly disordered ZnO films by surface-plasmon resonance, Appl. Phys. Lett. 90(23): 231106.

Akhavan, O.; Ghaderi, E. (2010). ACS Nano 4, 5731.

Chen, T.; Xing, G.Z.; Zhang, Z.; Chen, H.Y. and Wu, T. (2008). Tailoring the photoluminescence of ZnO nanowires using Au nanoparticles, Nanotechnology 19(43): 435711.

Cheng, P.H.; Li, D.S.; Yuan, Z.Z.; Chen, P.L. and Yang, D. (2008). Enhancement of ZnO light emission via coupling with localized surface plasmon of Ag island film, Appl. Phys. Lett. 92(4): 041119.

Dougami, N. and Takada, T. (2003). Modification of metal oxide semiconductor gas sensor by electrophoretic deposition, Sensors and Actuators B: Chemical 93: 316–320.

Fan, Y. (2017). Synthesis of Graphene and Graphene-Based Composite Membrane, Mechanical (and Materials) Engineering --Dissertations, Theses, and Student Research.

Ferrari, A.C.; Bonaccorso, F.; Fal'ko, V.; Novoselov, K.S., Roche S., BøggildP., Borini S., Koppens F.H.L., Palermo V., Pugno N., Garrido J.A., SordanR., Bianco A., Ballerini L., Prato M., Lidorikis E., Kivioja J., Marinelli C.,Ryhänen T., Morpurgo A., Coleman J.N., Nicolosi V., Colombo L., FertA., Hernandez M.G., Bachtold A., Schneider G.F., Guinea F., Dekker C.,Barbone M., Sun Z., Galiotis C., Grigorenko A.N., Konstantatos G., Kis A., Katsnelson M., Vandersypen L., Loiseau A., Morandi V., Neumaier D., Treossi E., Pellegrini V., Polini M., Tredicucci A., Williams G.M.,Hong B.H., Ahn J.H., Kim J.M., Zirath H., Wees van B.J., Zant van der H.,Occhipinti L., Di Matteo A., Kinloch I.A., Seyller T., Quesnel E., Feng X.,Teo K., Rupesinghe N., Hakonen P., Neil S.R.T., Tannock Q., Lowlander T.,Kinare J. (2015). Nanoscale, 7: 45.

Hassan, M.A. (2012). Preparation and characterization ZnO nanoparticles and study of morphology at high temperature, Iraqi Journal of Physics, 10(18): 17-23.

Lai, C.W.; An, J. and Ong, H.C. (2005). Surface-plasmon-mediated emission from metal-capped ZnO thin films, Appl. Phys. Lett. 86(25): 251105.

Mishra, S. and Hansora, D. (2018). Graphene Nanomaterials Fabrication, Properties and Applications, For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Copyright © 2018 by Pan Stanford Publishing Pte. Ltd.

Mohammedi, E.; Aliofkhazraei, M.; Sabour Rouhaghdam, A. (2017). In-situ study of electrophoretic deposition of zinc oxide nanosheets and nanorods, Department of Materials Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran Ceramics International, 44: 1471–1482.

Schedin, F.; Geim, A.K.; Morozov, S.V.; Hill, E.W.; Blake, P.; Katsnelson, M.I. and Novoselov, K.S. (2007). Detection of individual gas molecules adsorbed on graphene, Nat. Mater. 6(9): 652–655.

Singh, M.; Goyal, M. and Devlal, K. (2018). Size and shape effects on the band gap of semiconductor compound nanomaterials" Department of Physics and Electronics, National University of Lesotho, P.O. Roma 180, Roma, Lesotho, 12(4): 470–475

Wang, X.; Zhi, L.J.; Tsao, N.; Tomović, Z.; Li, J.L. and Müllen, K. (2008). Transparent carbon films as electrodes in organic solar cells, Angew. Chem. Int. Ed. Engl. 47(16): 2990–2992.

Yanning, Y.; Zhiyong, Z.; Junfeng, Y.; Qiaoping, L.; Fuchun, Z. and Weixia, L. (2015). Study on field emission characteristics of Ti-based chrysanthemum-like nano-ZnO cathode by electrophoresis deposition, Rare Met. Mater. Eng. 44: 2711–2715.

You, J.B.; Zhang, X.W.; Fan, Y.M.; Qu, S. and Chen, N.F. (2007). Surface plasmon enhanced ultraviolet emission from ZnO films deposited on Ag Si (001) by magnetron sputtering, Appl. Phys. Lett. 91(23): 231907.

Zhang, Y.; Zhang, Y.; Guo, Y.; Lingnan, Wu; Liua, Y. and Songa, L. (2019). Synthesis of AuPd nanoparticle-decorated graphene-coated ZnO nanorod arrays with enhanced photoelectrochemical performance and stability, Key Laboratory of Inorganic Coating Materials CAS, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, China.

Zhang, Y.P.; Li, H.B.; Pan, L.K.; Lu, T. and Sun, Z. (2009). Capacitive behavior of graphene–ZnO composite film for supercapacitors, J. Electroanal. Chem. 634(1): 68–71.