

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Structural and optical properties of Zinc oxide-Reduced Graphene oxide nanocomposite thin films prepared by hydrothermal method.

Guru Nisha Narayanan¹, Gokula Deepan.P¹, Dr.A.Karthigeyan^{1*}

¹Department of Physics and Nanotechnology, SRM University, Kattankulathur, Tamil Nadu, India.

Abstract: In this work, we report the synthesis and characterization of Zinc oxide– Reduced Graphene oxide Nanocomposite thin films prepared by hydrothermal route. The synthesized films were characterized by Scanning electron microscope (SEM), X-Ray Diffraction (XRD) and UV-VIS Spectrophotometer for morphology, structural and optical properties. The functional group analysis of Graphene Oxide was carried out using FTIR spectroscopy. The influence of amount of GO in the reaction medium on the surface morphology, structural and optical properties were investigated. It was found that the amount of GO showed negligible change in the morphology of the thin films but the bandgap changed from 3.3eV to 3eV.

Keywords: Nanocomposite thin films, Zinc Oxide, Graphene Oxide, hydrothermal method.

Introduction

Zinc Oxide (ZnO), a wide band gap (3.37eV) and with large exciton binding energy (60meV)¹ is a promising material for various applications such as gas sensors², solar cells³, UV sensor⁴. By addition of additives like GO showed enhanced properties in applications like gas sensor⁵ and UV sensor⁶. Graphene, a two dimensional honeycomb lattice structure with zero band gap has unique electrical, thermal and mechanical properties⁷⁻⁸ finds potential applications in solar cells⁹⁻¹¹, drug delivery¹² and sensors¹³. Various deposition methods such as chemical vapor deposition¹⁴⁻¹⁵ spray deposition¹⁶⁻¹⁷ and spin coating¹⁸⁻¹⁹ have been employed to deposit ZnO-RGO films over various substrates. Several works have been reported about ZnO–RGO nanocomposites such as MajidAzarang et.al synthesised ZnO/RGO nanocomposites and investigated the effect of GO concentration on photo current generation²⁰. N.M.Huang et.al prepared ZnO nanorods decorated RGO nanocomposites and studied the effect of GO concentration on morphology, structural and optical properties²¹. U. Alver et.al has studied optical and structural properties of ZnO nanorods grown on graphene oxide and reduced graphene oxide by hydrothermal process²².

In the present work a simple sol-gel technique was used to synthesize ZnO nanoparticles and GO was prepared by Hummers method. The ZnO-RGO nanocomposite thin films were prepared on glass substrate by spin coating technique and the prepared thin films were immersed vertically in aqueous growth solution containing zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 5H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$) and GO inside the Teflon – lined autoclave. The effect of different concentration of GO on morphology, structural and optical properties of ZnO-RGO nanocomposite thin films were investigated.

Experimental section

Preparation of Graphene Oxide:

Graphene oxide (GO) was synthesized from graphite powder by Hummers method. Briefly, 2 g graphite powder and 1g NaNO₃ were mixed with 46 mL of concentrated H₂SO₄. Next, 6 g of KMnO₄ was added under ice bath to prevent the temperature from exceeding 20°C, after which the mixture was stirred and held at 35°C for 30min. Then, 92mL of deionized water was slowly added into the system. After stirring for 15 min, 80mL of warm water was added. To reduce excess KMnO₄, a proper amount of 3% H₂O₂ aqueous solution was dropped into the mixture until no bubbles were observed. The mixture was then centrifuged to remove the residual impurities. The Graphitic oxidewas obtained by dehydration at 60°C in air. The GO is obtained by Graphitic oxide dispersed into water by ultra sonication and centrifugation for half an hour to remove any unexfoliated GO.

Seed layer Deposition

The seed layer was prepared by low cost sol gel technique. Prior to the seed layer deposition, the glass substrate (2" *2") were cleaned using chromic acid solution and then rinsed with de-ionized (DI) water. Further, the glass substrates were ultrasonically cleaned using acetone for 10 minutes. The cleaned glass substrates were then used for the deposition of ZnO-GO seed layer using spin coating technique. 0.9M Zinc Acetate dehydrate (Zn(CH₃COO)₂.H₂O, Merck 99.9%) dissolved in 15ml of 2-propanol and monoethanolamine (HOCH₂CH₂NH₂, Merck 99.9%) which was used as a stabilizer was added drop wise to yield a clear solution. The above solution was stirred for 1 hour. The molar ratios of Zinc Acetate dehydrate and Monoethanolamine were maintained at 1:1. The solution was then aged overnight to yield a homogeneous component. Various concentration of Graphene Oxide solution (1 wt.%, 3 wt. % and 5 wt.%) were prepared by dispersing the GO into distilled water through ultrasonication. The samples were then spin coated with graphene oxide and zinc solution at 3000 rpm for 30sec and annealed at 300° C for 10 mins for each deposition to remove organic residuals that might be present on the thin films.

Growth of Nanocomposite ZnO thin films through hydrothermal method

Zinc nitrate hexahydrate (Zn(NO₃)₂·5H₂O) and hexamethylenetetramine (HMTA), (C₆H₁₂N₄) purchased from Sigma-Aldrich were used as reagents. Nanocomposite ZnO-GO thin films were formed by immersing the prepared ZnO-GO thin films vertically in aqueous growth solution containing zinc nitrate hexahydrate and HMTA in 50ml double distilled water, inside the Teflon – lined autoclave at 90° C for 3 hours. The molar ratio of ZN/HMTA is 1:1. The obtained thin films were thoroughly washed with de-ionized water to remove any residual materials and then annealed at 350° C for 1 hour. The samples were named as S1, S2 and S3 respectively.

The morphology of ZnO-RGO nanocomposite thin films were examined with Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) analysis were performed using FEI Quanta FEG 200. The structure of the thin film was analyzed by PANalytical'sX'Pert PRO with Cu K α radiation ($\lambda = 1.542\text{\AA}$). The functional group analysis of graphene oxide was studied using Fourier Transform Infrared Spectroscopy using ALPHA-T FT-IR Spectrometer. Optical absorption spectra were investigated using SHIMADZU UV-Vis-Spectrophotometer.

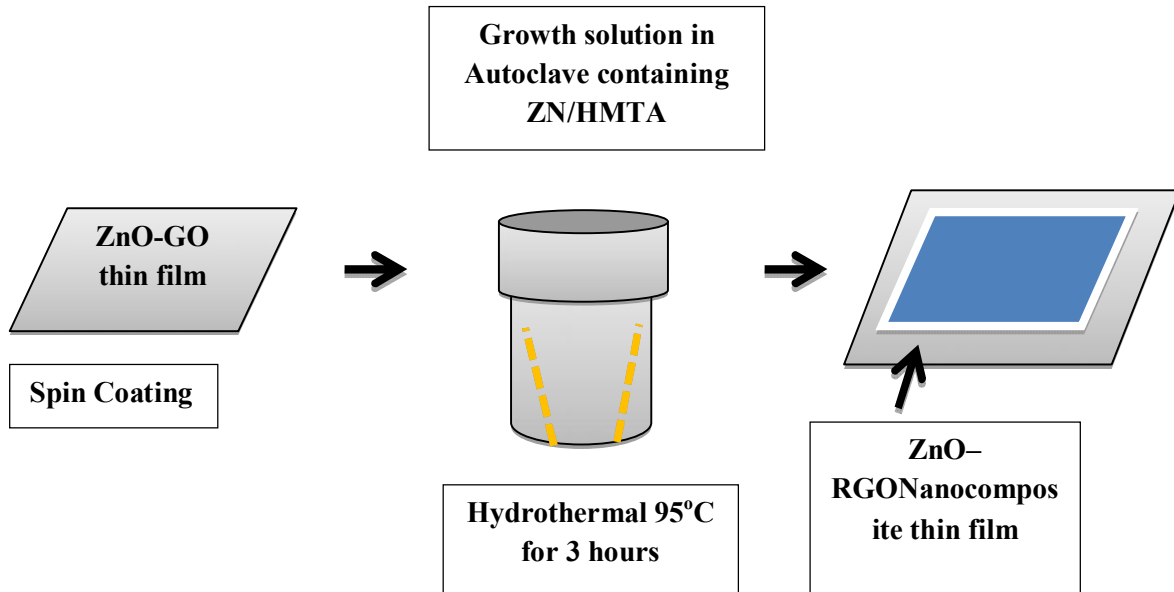


Fig.1 Illustration for preparation of ZnO-RGO nanocomposite thin film through a hydrothermal process.

Results and discussion

Fig.2 shows FESEM images of ZnO-RGO nanocomposite thin films (a-c) with different GO concentration. It is observed that the surface of GO is packed densely with ZnO nanoparticles. It is seen that as the GO concentration is increased from 1 wt. % to 5 wt. %, agglomeration of particles occurs which might be due to the increase in the GO concentration Fig.2 (d) shows the EDS analysis of the product. It indicates that the ZnO-RGO nanocomposite thin films are composed of three elements: C, Zn and O and absence of other impurities.

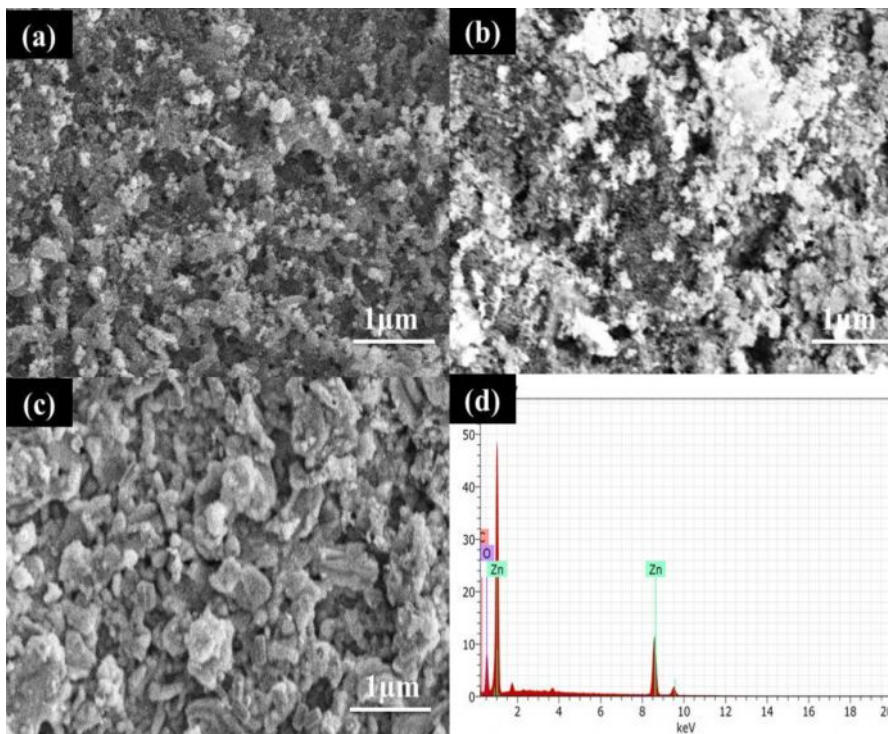


Fig.2 Surface Morphology of ZnO-RGO nanocomposite thin films prepared by hydrothermal method with GO Concentration a) 1 wt. % b) 3 wt. % c) 5 wt. % and EDS spectra (d) of 5 wt. % GO in ZnO-RGO nanocomposite thin films

The XRD pattern of GO is shown in fig 3 (a). The GO shows the diffraction peak at $2\theta = 11.3^\circ$. The ZnO-RGOnanocomposite thin films are shown in fig 3 (b).

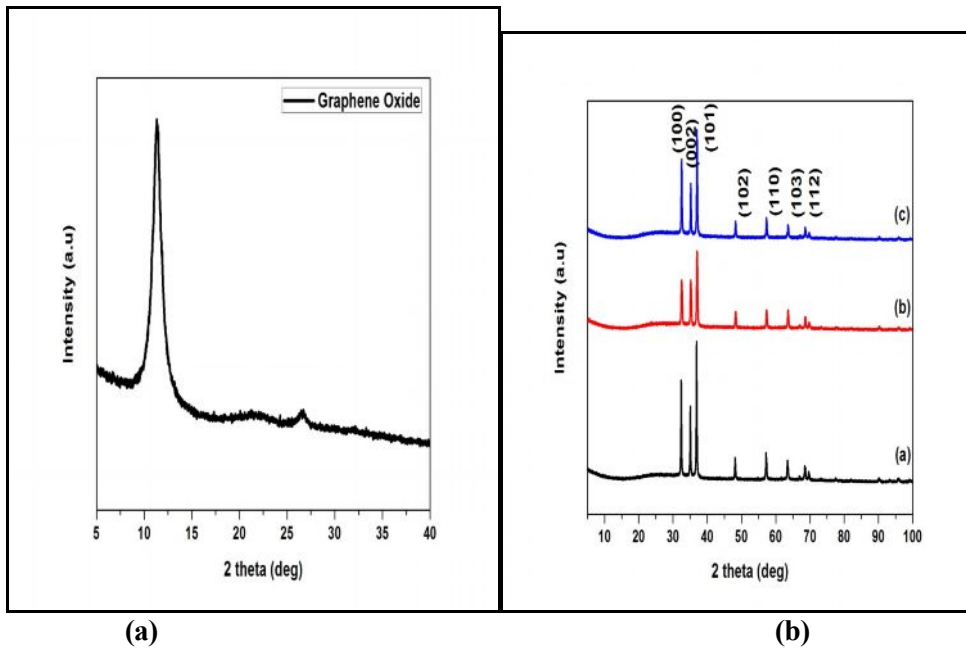


Fig.3 XRD pattern of (a) GO and (b) with GO Concentration a) 1 wt. % b) 3 wt. % c) 5 wt. %

The diffraction peak at 32° , 36° , 48° , 57° , 63° and 68° corresponds to (100), (002), (101), (102), (110), (103) and (112). There is no characteristic diffraction peak of GO observed indicating the reduction of GO to RGO by hydrothermal process and formation of high purity of ZnO film²³. No diffraction peak of GO could also be due to relatively low content of GO in ZnO-RGOnanocomposite thin films²⁴. It can be also observed that as the concentration of GO increases from 1 wt. % to 5 wt. %, the peak intensity reduces which could possibly due to the reduction of ZnO amount in the composite²⁰.

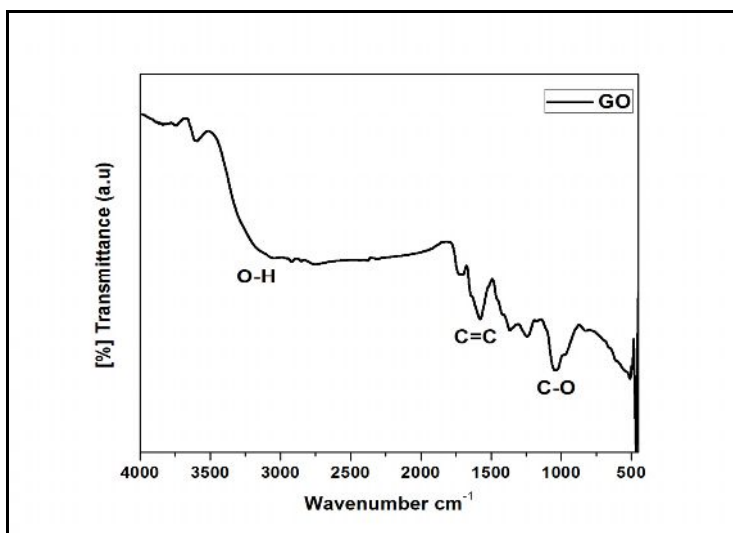


Fig.4FTIR Spectra of GO

Fig. 4 shows the FTIR spectra of GO. Mainly GO has carboxyl and hydroxyl groups in it. The broad peak at 3107 cm^{-1} represents O-H stretching vibrations. The peaks at 1579 cm^{-1} and 1049 cm^{-1} represents C=C stretching vibrations and C-O stretching vibrations²⁵.

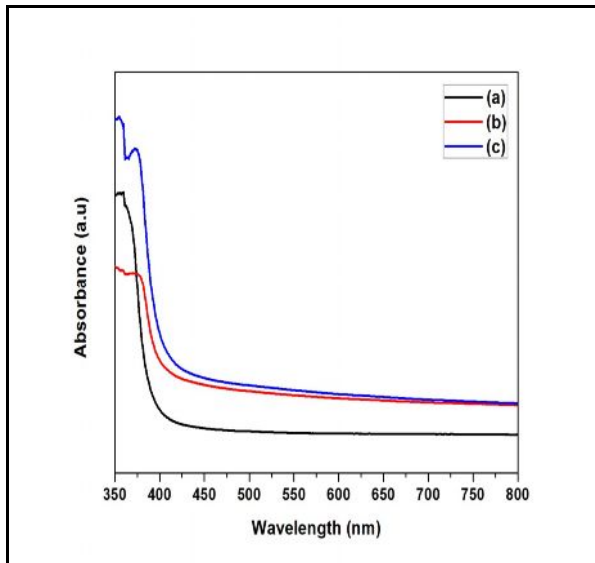


Fig.5 UV-visible spectra of the synthesized ZnO-RGO nanocomposite thin films with GO Concentration a) 1 wt. % b) 3 wt. % c) 5 wt. %

Fig. 5 shows the UV-visible spectra of the synthesized ZnO-RGO nanocomposite thin films with various concentration of GO. The absorption edge of ZnO-RGO nanocomposite thin films shows a slight red-shift towards the higher wavelength with the increase of GO content which could probably be due to the chemical bonding between ZnO and GO²⁶.

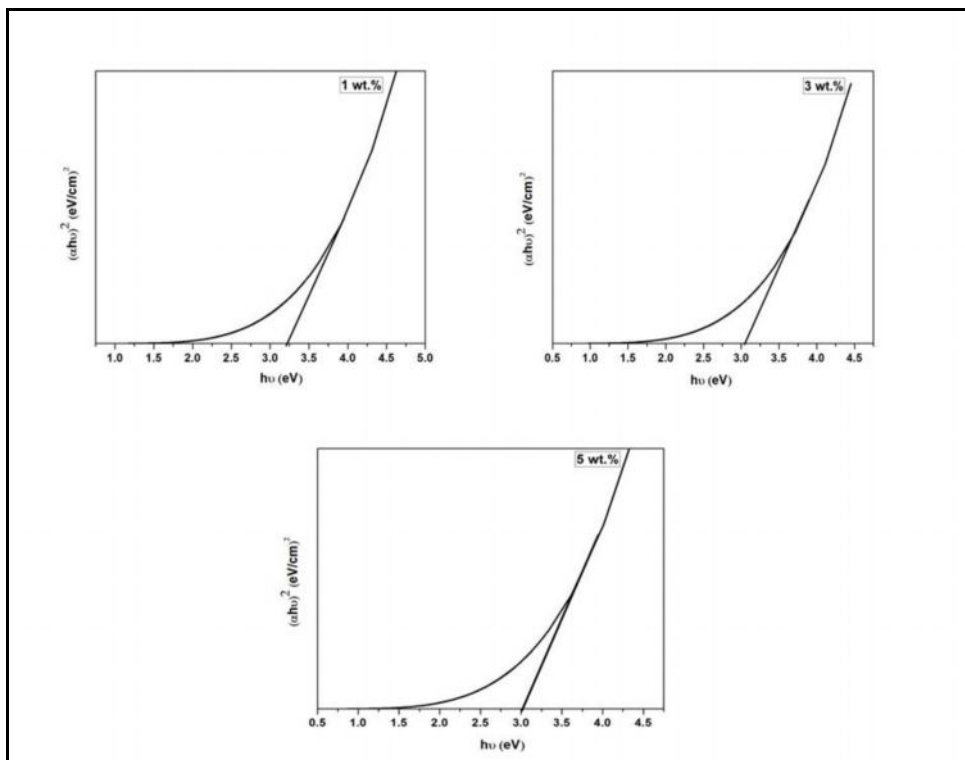


Fig.6. Direct bandgap of ZnO-RGO nanocomposite thin films with GO Concentration a) 1 wt. % b) 3 wt. % c) 5 wt. % by using Tauc's plot

Tauc's plot of ZnO-RGO nanocomposites thin films with various concentration of GO is shown on Fig 6. The estimated band gap values of the samples are about 3.33 eV, 3.28 eV and 3.0 eV corresponding to 1 wt. %, 3 wt. % and 5 wt. % of GO. This indicates that there is a band gap narrowing of ZnO due to the introduction of GO in the matrix of ZnO nanoparticles²⁷ and the formation of Zn-O-C chemical bond in the composites²⁸.

Conclusion

In summary, we have prepared ZnO-RGOnanocomposite thin films by hydrothermal method. The effects of GO concentration on morphology, structural and optical proprieties are investigated. It is seen that the addition of GO does not change the morphology of ZnO thin films. The XRD patterns states that there is no diffraction peak of GO which could also be due to relatively low content of GO in nanocomposite. Futhermore, the bandgap of ZnO nanoparticles is decreased by addition of GO and slight red shift towards the higher wavelength could be investigated.

Acknowledgements

The authors would like to thank SRM University, Chennai for the award of SRM fellowship to carry out the research work. We also thank DST – FIST (DST – FIST – SR/FST/PSI-155/2010) for experimental facility, Nanotechnology Research Center, SRM University, Chennai for extending the characterization facilities. The authors would also like to acknowledge Prof. D. John Thiruvadigal, Head, Department of Physics and Nanotechnology, SRM University, Chennai, Dr.K.Ramamurthi, Mr.V.Pandiyarasan and Mr.J.Jerryfor valuable suggestions and moral support.

References

1. Minggang, Li., Hari-Bala, Xiaotang, L., Xiaokun, M., Fang, S., Lanqin, T. and Zichen, W., Direct synthesis of monodispersed ZnO nanoparticles in an aqueous solution, *Mater Lett*, 2007, 61, 690-693.
2. Tian, S., Yang, F., Zeng, D., Xie, C., Solution-processed gas sensors based on ZnOnanorods array with an exposed (0001) facet for enhanced gas-sensing properties, *Journal of Physical Chemistry C*, 2012, 116, 10586-10591.
3. Kim, K.S., Song, H., Nam, S.H., Jeong, H., Kim, W.B., Kim, S.M. and Jung, G.Y., Fabrication of an Efficient Light-Scattering Functionalized Photoanode Using Periodically Aligned ZnO Hemisphere Crystals for Dye-Sensitized Solar Cells, *Advanced Materials*, 2012, 24, 792-798.
4. SuoBai , Weiwei, W., Yong, Q., Nuanyang, C., Dylan, J.B., and Xudong, W., High-Performance Integrated ZnO Nanowire UV Sensors on Rigid and Flexible Substrates, *Adv. Funct. Mater.*, 2011, 1-6.
5. Sen, L., Bo Y., Hao, Z., Teng, F. and Zhang, T., Enhancing NO₂ gas sensing performances at room temperature based on reduced graphene oxide-ZnO nanoparticles hybrids, *Sensors and Actuators B*, 2014, 202, 272-278
6. Haixin, C., Zhenhua, S., Keith Yat-Fung, H., Xiaoming, T., aFeng, Y., Wai-Ming, K. and Zijian Z., A highly sensitive ultraviolet sensor based on a facile in situ solution-grown ZnOnanorod/ graphenehetero structure, *Nanoscale*, 2011, 3, 258-264.
7. Balandin, A.A., Ghosh, S., Bao, W.Z., Calizo, I., Teweldebrhan, D., Miao, F. and Lau, C., Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.*, 2008, 8, 902-907.
8. Li, D., Muller, M.B., Gilje, S., Kaner, R.B. and Wallace, G.G., Processable aqueous dispersions of graphenenanosheets, *Nature Nanotechnol.*, 2008, 3, 101-105.
9. Sun, T., Wang, Z.L., Shi, Z.J., Ran, G.Z., Xu, W.J., Wang, Z.Y., Li, Y.Z., Dai, L. and Qin, G.G., Multilayered graphene used as anode of organic light emitting devices, *Appl. Phys. Lett.*, 2010, 96, 133301-1-133301-3.
10. Xu, Y., Long, G., Huang, L., Huang, Y., Wan, X., Ma, Y. and Chen, Y., Polymer photovoltaic devices with transparent graphene electrodes produced by spin-casting, *Carbon* 2010, 48, 3293-3311.
11. Yin, Z.Y., Sun, S., Salim, T., Wu, S., Huang, X., He, Q., Lam, Y.M. and Zhang, H., Organic photovoltaic devices using highly flexible reduced graphene oxide films as transparent electrodes, *ACS Nano*, 2010, 4, 5263-5268.
12. Sun, X., Liu, Z., Welsher, K., Robinson, J.T., Goodwin, A., Zaric, S. and Dai, H., Nano-Graphene Oxide for Cellular Imaging and Drug Delivery, *Nano Res.*, 2008, 1, 203-212.
13. Sen, L., Bo, Y., Hao, Z., TengFei, and Tong Z., Enhancing NO₂ gas sensing performances at room temperature based on reduced graphene oxide-ZnO nanoparticles hybrids, *Sensors and Actuators B*, 2014, 202, 272-278
14. Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V., Dresselhaus, M.S, Kong, J., Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition, *Nano Lett.*, 2009, 9, 30-35.

15. Bae, S., Kim, H., Lee, Y., Xu, X., Park, J.S., Zheng, Y., Balakrishnan, J., Lei, T., Kim, H.R., Il Song, Y., Kim, Y.J., Kim, K.S., Özyilmaz, B., Ahn, J.H., Hong, B.H., Iijima, S., Roll-to-roll production of 30-inch graphene films for transparent electrodes *Nat. Nanotechnol.*, 2010, 5, 574–578.
16. Blake, P., Brimicombe, P.D., Nair, R.R., Booth, T.J., Jiang, D., Schedin, F., Ponomarenko, L.A., Morozov, S.V., Gleeson, H.F., Hill, E.W., Geim, A.K. and Novoselov, K.S., Graphene-based liquid crystal device, *Nano Lett.*, 2008, 8, 1704–1708.
17. Pham, V.H., Cuong, T.V., Hur, S.H., Shin, E.W., Kim, J.S., Chung, J.S. and Kim, E.J., Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating, *Carbon*. 2010, 48, 1945–1951.
18. Watcharotone, S., Dikin, D.A., Stankovich, S., Piner, R., Jung, I., Dommett, G.H.D., Evmenenko, G., Wu, S.E., Chen, S.F., Liu, C.P., Nguyen, S.B.T. and Ruoff, R.S., Graphene–Silica Composite Thin Films as Transparent Conductors, *Nano Lett.*, 2007, 7; 1888–1892.
19. Wu, S., Yin, Z., He, Q., Lu, G., Zhou, X. and Zhang, H., Electrochemical deposition of Cl-doped n-type Cu₂O on reduced graphene oxide electrodes *J. Mater. Chem.*, 2011, 21, 3467–3470.
20. MajidAzarang Ahmad, S., Ramin, Y., and Sookhajian, M., Effects of graphene oxide concentration on optical properties of ZnO/RGO nanocomposites and their application to photocurrent generation, *Journal of Applied Physics*, 2014, 116, 084307-1-084307-6.
21. Marlinda, A.R., Huang, N.M., Muhamad, M.R., An'amt, M.N., Chang, B.Y.S., Yusoff, N., Harrison, I., Lim, H.N., Chia, C.H. and Vijay Kumar, S., Highly efficient preparation of ZnO nanorods decorated reduced graphene oxide nanocomposites, *Materials Letters*, 2012, 80, 9–12.
22. Alver, U., Zhou, W., Belay, A.B., Krueger, R., Davis, K.O. and Hickman, N.S., Optical and structural properties of ZnO nanorods grown on graphene oxide and reduced graphene oxide film by hydrothermal method, *Applied Surface Science*, 2012, 258, 3109–3114.
23. Chen, S., Zhu, J., Wu, X., Han, Q. and Wang, X., Graphene Oxide–MnO₂ Nanocomposites for Supercapacitor, *ACS Nano*, 2010, 4, 2822-2830.
24. Yun Hau, N., Ian, V., Lightcap, Kevin, G., Michio, M. and Prashant, V. K., To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO₂ Nanostructured Films?, *J. Phys. Chem. Lett.*, 2010, 1, 2222-2227.
25. Hummers, W.S. and Offeman, R.E., Preparation of Graphitic Oxide, *J. Am. Chem. Soc.*, 1958, 80, 1339.
26. Huang, K., Li, Y.H., Lin, S., Liang, C., Wang, H., Ye, C.X., Wang, Y.J., Zhang, R., Fan, D.Y., Yang, H.J., Wang, Y.G. and Lei, M., A facile route to reduced graphene oxide–zinc oxide nanorod composites with enhanced photocatalytic activity, *Powder Technology* 2014, 257, 113–119
27. Zhang, C., Nan, Z. and Yi-Jun, X., Synthesis of graphene–ZnO nanorod nanocomposites with improved photoactivity and anti-photocorrosion, *CrystEngComm*, 2013, 15, 3022-3030.
28. Zhang, H., Lv, X., Li, Y., Wang, Y. and Li, J., P25-graphene composite as a high performance photocatalyst, *ACS Nano*, 2009, 4, 380–386.
