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*Short Communication*

# Performance of Dye-Sensitized Solar Cell Utilizing Ga-ZnO Nanorods: Effect of Ga Concentration

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Ga-doped ZnO nanorods with various Ga concentration have been successfully grown on the surface of the FTO (Fluorine Tin Oxide) substrate using hydrothermal method that was achieved by varying the gallium nitrate hydrate precursor concentration during the growth reaction containing zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMTGallium nitrate hydrate (GNH) concentration used were 2, 3, 5, 6 and 10% of the ZnO precursor solution. The FESEM analysis on the sample indicated that the nanostructures were vertically oriented nanorods. While XRD analysis confirmed that the Ga-ZnO was successfully prepared using the present approach and the Ga content in the Ga-ZnO nanorods can be simply varied by suing different concetration of Ga precursor during the growth process. Current-voltage analysis on the dye sensitized solar cell (DSSCs) containing Ga-doped ZnO nanorods as photoanode with structure of FTO/Ga-doped ZnO/Dye/Electrolyte/Platinum indicated that the performance of the device increased with the increasing of Ga concentration in the ZnO nanorods and optimum if using Ga precursor concentrration of 5%. At this condition the efficiecy was as high as 0.362%. It is nearly three times higher compared to device utilizing pure ZnO nanorods (0.132%). The performance decreased when the Ga concentration further increased in the nanorods. Enhancement of the device performance upon doped with the Ga is associated with the decreasing of carrier-recombination as judged from the dark current analysis results.

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**Keywords:** Gallium dope; Dye Sensitized Solar Cells; ZnO Nanorods; Hydrothermal method

## 1. INTRODUCTION

ZnO nanostructures has been receiving continuos attention for various the technological applications ranging from optoelecronics, solar cell, catalysis and sensors [1-5]. Physical properties of ZnO nanostructures, including electrical and optical properties, nanostructure shape and morphology has been continuously engineered to obtain excellent performance in applications. Metal doping has been well-known as versatile approach to modify the electrical and optical properties of ZnO nanostructures [1]. Introduction of metal into the ZnO lattice induces modification in the density of state of outermost orbital and the Fermi level, leading to enhanced photo activity of the materials [6, 7]. Ga is amongst the transition metal that has been widely used to modify photo activity and optoelectronic properties of wide range of semiconducting oxides and other semiconductors [8, 9]. For example, the photo activity of TiO2 nanostructure has been improved for several order higher when the Ga is introduced into the TiO2 lattice. Dark current of amorphous silicon has been effectively decrease when the Ga is introduced into the crystal [10]. Still many peculiar properties are generated by the Ga doping, including lattice-mismatching morphology modification, enhanced surface chemistry properties, etc [11, 12]. Therefore, Ga doping effect on the ZnO nanostructure properties should be continuously experimented in order to obtain unusual performance in applications.

This paper reports the study of the effect of Ga doping on the photovoltaic performance of ZnO nanorods. Hydrothermal method was used to growth the Ga doped-ZnO nanostructures. In typical procedure, we found that the Ga doping into the ZnO nanostructure has effectively improved the photo activity of the ZnO. Improvement of power conversion efficiency up to three times were observed in a DSSC device when using Ga doped-ZnO nanorods. The decreasing in the carrier recombination due to facile transport is considered as the main reason for the improvement of the solar cell. The Ga doped-ZnO preparation ad dye-sensitized solar cell characterization will be discussed.

## 2. EXPERIMENTAL

Growth of ZnO nanostructures onto FTO substrate was prepared via hydrothermal method through 2 step processes, namely seeding and growth process [13]. In the seeding process, ZnO nanoseeds were coated on the FTO substrate by using our previously reported method, namely alcohol-thermal seeding method. Briefly, the process was started by forming a thin layer of ethanolic solution of 10 mM on a FTO by using spin-coating process at 3000 rpm for 30 seconds. The sample was then dried at 100 $^{o}$C on a hot-plate for 15 minutes and then cooled down to 60$^{o}$C. These procedures were repeated for three times in order to get appropriate density of ZnO nanoseeds on the FTO substrate surface. Finally, the sample was annealed at 350$^{o}$C for 1 hour. From this approach, high-density Zno nanoseed of size approximately 5 nm can be prepared on the surface.

The ZnO nanorods were then grown up from this nanoseeds by by immersing the ZnO nanoseeds-attached FTO into a a growth solution, namely a mix solution of 0.1 M ZNH and 0.1 M HMT. In order to achieve the Ga doping in the Zno nanorods, gallium nitrate hydrate (purchased from Sigma Aldrich, USA) with concentration of 2 to 10 % of ZnO precursor concentration into the growth solution. The growth process was carried out at 90 $^{o}$C for 8 hours inside an electrical oven. Finally, the samples were annealed at 250 °C for 30 minutes in a furnace.

The morphology of the samples was observed using FESEM technique of Zeiss Supra 55VP. The elemental analysis was performed by using energy dispersive x-ray (EDX) spectrometer. X-ray diffraction (XRD) method was carried out in order to examine the structure and phase structure of the

ZnO nanostructures using diffractometer model Bruker D8 Advance. The optical properties of the sample was evaluated using UV-Vis spectrophotometer (Lambda 900 Perkin Elmer).

A DSSC was fabricated by arranging the sandwich structure of ZnO and the platinum counter electrode. A parafilm was used as spacer. Prior to the DSSC fabrication, the Ga-doped ZnO nanostructures were immersed into 0.3 mM N719 dye solution for 2 hours. The electrolyte was then injected into the cell. The electrolyte used was Iodolyte, namely an electrolyte that contained a redox couple of iodide/triiodide. It was purchased from Solaronix, Switzerland. The performance of the DSSC was examined by observing the I-V characteristics in the dark and under illumination of solar simulator with an intensity of 100 mW cm$^{-2}$ (AM1.5). I-V curves were recorded by a Keithley high-voltage source model 237.

## 3. RESULTS AND DISCUSSION

The XRD spectra of ZnO nanorods doped with various concentration of Ga precursors, namely 2 to 10% wt are shown in Figure 1. The figure shows that three diffraction peaks at 34.56, 36.36 and 47.68° were observed in the spectra. The spectra agree with the standard diffraction data JCPDS file no. 01-070-8070, where the three diffraction peaks are attributed to (002), (101) and (102) planes, respectively. The XRD analysis confirms that the peak intensity at (002) is the strongest, inferring the hexagonal phase of the ZnO nanorods, which grows along the c-axis . As also can be seen from the figure and its inset, the main diffraction peaks of (002) significantly shifted to a higher angle upon doping with the Ga ion. The shift increases with the increasing of Ga precursor concentration. This reveals that there is a lattice constraint process in the ZnO lattice upon doped with the Ga [14]. This is due to the ionic radius of the Ga is little bit bigger compared to Zn so that substitution of Ga induces significant stress to the host lattice. The full-width at half maximum (FWHM) and crystalline-size for each sample were measured and calculated using EVA Diffract Plus as listed in Table 1. As can be seen from the table 1, the FWHM of diffraction peak increases as the GNH percentage increases from 2 to 5% and then it decreases as the GNH percentage increase to 10%. On the other hand, crystalline size decreases as Ga-percentage increases from 2 to 5% and then it increases when the Ga-percentage increase to 10%. No diffraction peaks related to fcc phase of Ga is observed in the spectra, reflecting the effective substitution of Ga ion into the ZnO lattice.

**Table 1.** FWHM and crystalline-size of highest XRD peak at various GNH-percentages in the growth solution

| Sample (% wt) | 2 | 3 | 5 | 6 | 10 |
|---|---|---|---|---|---|
| FWHM (deg) | 0.177 | 0.182 | 0.204 | 0.195 | 0.179 |
| Crystalline-size (nm) | 46.88 | 45.6 | 40.68 | 42.56 | 46.36 |

Figure 2 shows the FESEM micrographs of the Ga-doped ZnO nanostructures synthesized at various concentration of Ga precursors. It can be seen from the images that the morphology, diameter and the nanorod growth density of all samples are relatively unchanged with the variation of Ga concentration. The diameter of the ZnO nanorods is about 200 nm for all samples. Similarly, the thickness of the nanorod is also about the same, namely approximately 1100 nm. This condition should be suitable to see the effect of the Ga doping on the photoactivity of the ZnO nanorods.

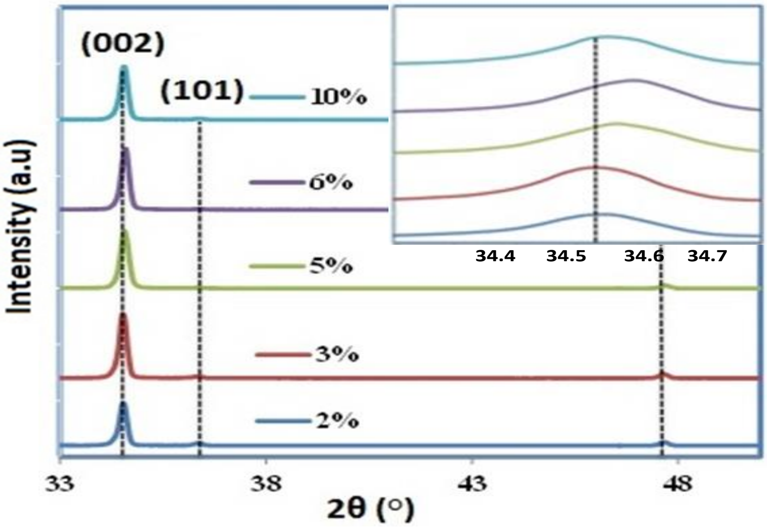

**Figure 1.** XRD spectra of Ga-doped ZnO nanostructures with various Ga precursor concentration. The inset shows the detailed shifting at (002) peak.

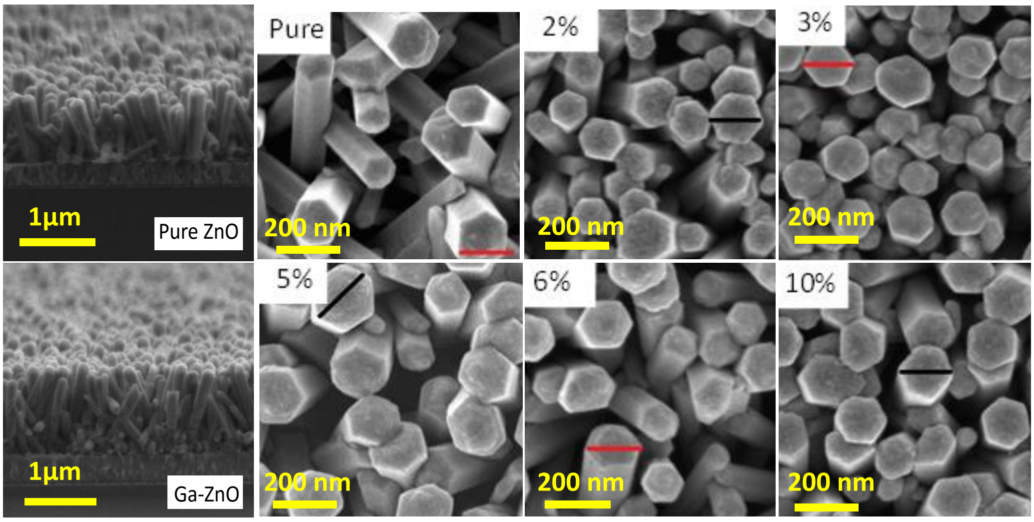

**Figure 2.** FESEM micrographs of cross-sectional of the Pure and Ga-doped along with the surface morphology.

In order to verifying the existence of the Ga in the ZnO nanorods, elemental analysis was carried out using EDX spectroscopy. The result is shown in Figure 3. As can be seen from the Figure

3, the Ga element is exist in the spectrum with relatively higher atomic concentration, reflecting effective substitution of Ga atom into the ZnO lattice. Therefore, it can be worthwhile remarked that the presence method has successfully prepared the Ga-doped ZnO nanorods.

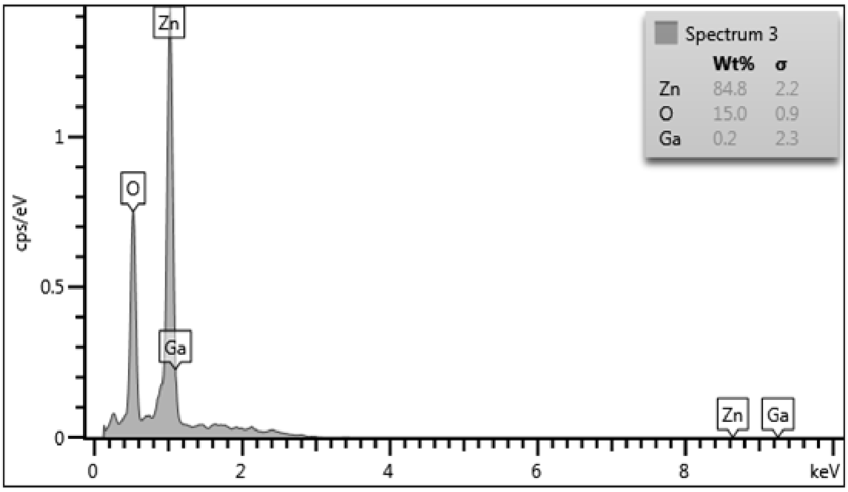

**Figure 3.** EDX spectrum of Ga-ZnO prepared using Ga precursor concentration of 3%.

DSSC was fabricated to examine the effect of Ga doping on the photoactivity of the ZnO nanorods by arranging the sandwich structure containing Ga-doped ZnO nanorods grown on FTO as a working electrode, electrolyte solution, and the platinum nanoparticles film grown on FTO as a counter electrode. Figure 4A shows the I-V characteristics of the DSSCs in dark condition using Ga-doped ZnO nanorods prepared at various Ga precursor concentration of 2, 3, 5, 6 and 10% wt. As noticed from the figure, the forward bias exhibits relatively high dark current flow at the bias of approximately 0.55 to 0.58 V. Despite this dark current performance is inferior to recently reported result, however, this characteristic is normal for case of DSSCs utilizing the ZnO as the photoactive materials. Therefore, it can be used to examine the effect Ga doping on the photoactivity of ZnO nanorods in DSSCs. Figure 4B is the typical J-V curves of the DSSCs device with Ga-doped ZnO nanorods photoanode of different Ga concentration under irradiation of simulated sun AM1.5 at 100 mWcm-2. The photovoltaic parameters are summarized in Table 2. As can be seen from both the figure and the table, the performance of the device increases with the increasing of Ga concentration in the ZnO nanorods and optimum at concentration of 3%. At this condition, the Jsc and Voc of the device are 1.87 mAcm-2 and 0.491 V, respectively. It is equivalent to a power conversion efficiency as high as 0.362%, which is three time higher compared to device utilizing pure ZnO nanorods (0.132%). The performance of the device does not further improve when the Ga concentration increases above 3%, but degrades instead.

It is true that the present device performance is still much low compared to DSSCs device utilizing TiO2 photoanode [15, 16]. It is due to the effect of not optimized dye-adosprtion onto the ZnO nanorods surface. In this study, the dye was deposited onto the Zno nanorods surface via spin-coating method, which may only transfer the dye to the outer surface of the nanorods. While the lower side of the nanorod is effectively uncovered by the dye molecules. Our analysis indicated that dipping method was not suitable for ZnO because the dye could corrode the ZnO nanostructure. Higher performance can be achieved if suitable method for dye deposition or new type of dye are obtained. The attempt to solve this problem is being pursued.

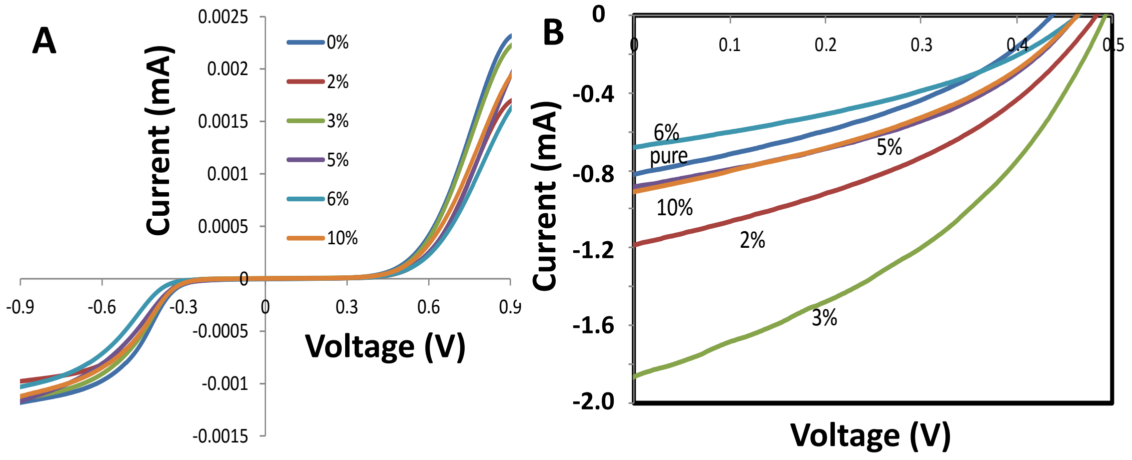

**Figure 4.** J-V characteristics of cells in dark (A) and under illumination of AM1.5 100 mW cm$^{-2}$ simulated sun light source (B).

The variation of device performance upon Ga doping can be associated with the improvement of the photoactivity and photosensitivity of the ZnO upon doped via defect density decreasing. As judged from the XRD spectra in Figure 1 that shows a dramatic shifting in the main diffraction peaks, there should be a massive modification in the electronics band density of state of ZnO, the result of charge transfer between the Ga and ZnO electronic state. On the basis of the UV-Vis absorption spectra of the Ga-doped ZnO shown in Figure 5, there could be the reduction of defect density in the ZnO nanocrystal upon doped with Ga as the decreasing of defect related absorbance in the ZnO samples, namely at the region of 400 to 650 nm. However, neither any indication of energy band gap modification nor improvement of sample absorbance upon doping.

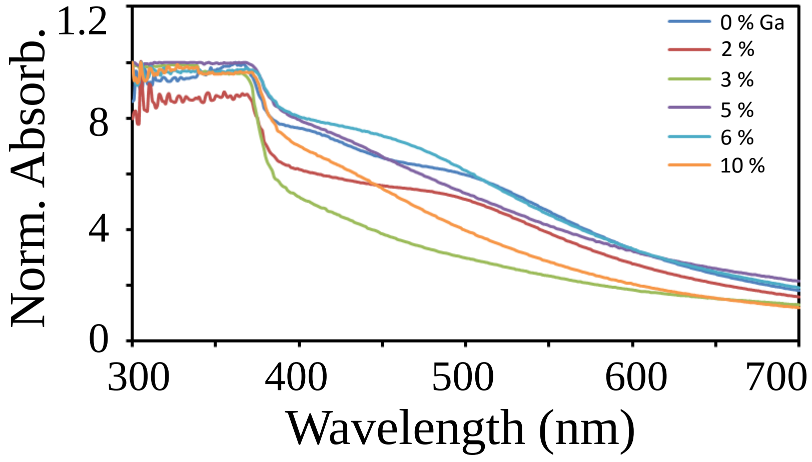

**Figure 5.** Normalized absorbance of Ga-doped ZnO nanorods with different Ga precursor concentration.

**Table 2.** Photovoltaic parameters of cells utilizing Ga-doped ZnO at different Ga precursor concentration.

| No | Ga-% | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | $\eta$ (%) |
|---|---|---|---|---|
| 1. | Pure | 0.435 | 0.82 | 0.132 |
| 2. | 2 | 0.482 | 1.18 | 0.220 |
| 3. | 3 | 0.491 | 1.87 | 0.362 |
| 4. | 5 | 0.461 | 0.88 | 0.163 |
| 5. | 6 | 0.463 | 0.68 | 0.117 |
| 6. | 10 | 0.463 | 0.91 | 0.158 |

## 4. CONCLUSIONS

The Ga-doped ZnO nanorods have been successfully synthesized using modified hydrothermal method. The XRD analysis indicates that there is a significant shifting to a bigger angle in the diffraction peak, particularly at (002) Bragg plane, reflecting a lattice constraining upon the substitution of Ga in the ZnO lattice. The doping is further verified by the EDX analysis. FESEM images shows that no change in the morphology of the nanorods upon Ga doping. XRD and UV-Vis spectroscopy analysis reveal that the Ga doping enhances the photosensitivity of the ZnO via the reduction of defect density in the nanocrystal system. This is manifested by the improvement of the DSSCs power conversion efficiency for several order upon the addition of Ga in the ZnO lattice, namely from 0.132 to 0.362%. The present performance is still relatively low compared to recent reported result because of dye adsorption onto the ZnO nanorods is not optimum. Higher performance will be obtained if suitable dye for ZnO is obtained.

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## References

1. X. Yu, T.J. Marks, A. Facchetti, *Nat Mater,* 15 (2016) 383.
2. Z. Qidong, Y. Miao, X. Tengfeng, P. Linlin, W. Ping, W. Dejun, *Nanotechnology*, 19 (2008) 245706.
3. J. Ebothe, I.V. Kityk, S. Benet, B. Claudet, K.J. Plucinski, K. Ozga, *Opt. Commun*., 268 (2006) 269.
4. K. Ozga, T. Kawaharamura, A. Ali Umar, M. Oyama, K. Nouneh, A. Slezak, S. Fujita, M. Piasecki, A.H. Reshak, I.V. Kityk, *Nanotechnology* 19 (2008) 185709.
5. Z.L. Wang, *Mater. Today,* 7 (2004) 26.
6. K. Ueda, H. Tabata, T. Kawai, *Appl. Phys. Lett*. 79 (2001) 988.
7. S. Singh, M.S.R. Rao, *Phys. Rev. B*, 80 (2009) 045210.

8. E. Della Gaspera, M. Bersani, M. Cittadini, M. Guglielmi, D. Pagani, R. Noriega, S. Mehra, A. Salleo, A. Martucci, *J. Am. Chem. Soc*., 135 (2013) 3439.
9. S.W. Glunz, S. Rein, J. Knobloch, W. Wettling, T. Abe, *Prog. Photovoltaics: Res. Appl*., 7 (1999) 463.
10. V. Gross, H.W. Grueningen, E. Niemann, R. Fischer, *J. Non-Cryst. Solids*, 97 (1987) 643.
11. J. Kim, G.V. Naik, A.V. Gavrilenko, K. Dondapati, V.I. Gavrilenko, S.M. Prokes, O.J. Glembocki, V.M. Shalaev, A. Boltasseva, *Phys. Rev. X*, 3 (2013) 041037.
12. R. Wang, A.W. Sleight, D. Cleary, *Chem. Mater*., 8 (1996) 433.
13. L. Vayssieres, Adv. Mater., 15 (2003) 464.
14. M.A. Pfeifer, G.J. Williams, I.A. Vartanyants, R. Harder, I.K. Robinson, *Nature*, 442 (2006) 63.
15. S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F.E. CurchodBasile, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, K. NazeeruddinMd, M. Grätzel, *Nat. Chem*., 6 (2014) 242.
16. A. Ali Umar, S. Nafisah, S.K. Md Saad, S. Tee Tan, A. Balouch, M. Mat Salleh, M. Oyama, *Sol. Energ. Mater. Sol. Cells*, 122 (2014) 174.

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