Gmail **Marjoni Imamora <marjoniimamora@gmail.com>**

Decision on your manuscript #JMSE-D-17-04705

1 message

Journal of Materials Science: Materials in Electronics (JMSE) Thu, Jan 4, 2018 at 5:56 PM
<em@editorialmanager.com>
Reply-To: "Journal of Materials Science: Materials in Electronics (JMSE)" <preethi.subramanian@springer.com>
To: Marjoni Imamora <marjoniimamora@gmail.com>

CC: fitriyennis@yahoo.com, akrajas@ukm.edu.my, mms@ukm.edu.my

Dear Dr Imamora:

REF: YOUR PAPER #JMSE-D-17-04705
"Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration"

Following our acknowledgement of your paper, I have now received the referee's report, which is appended below.

The referee considers that substantial modification is necessary before the paper can be accepted, and the report outlines what is necessary to be done.

When preparing your revised manuscript, you are asked to carefully consider the reviewer comments which are attached, and submit a list of responses to the comments. Your list of responses should be uploaded as a file in addition to your revised manuscript.

PLEASE NOTE: YOUR REVISED VERSION CANNOT BE SUBMITTED IN .PS OR .PDF. IN THE EVENT THAT YOUR REVISED VERSION IS ACCEPTED, YOUR PAPER CAN BE SENT TO PRODUCTION WITHOUT DELAY ONLY IF WE HAVE THE SOURCE FILES ON HAND. Submissions without source files will be returned prior to final acceptance.

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Please click "Author Login" to submit your revision.

We expect your revised paper to be submitted within 2 months, after which the paper will be withdrawn if we do not hear from you.

I look forward to hearing from you in due course.

With best wishes.

Yours sincerely,

Peter Capper, Editor, PhD
Journal of Materials Science: Materials in Electronics

COMMENTS TO THE AUTHOR:

Reviewer #1: Comments: The manuscript by Umar et.al reports the dependence of alignment ordering on precursor concentration in the hydrothermally grown process of well-aligned ZnONRs. They utilized XRD, UV-vis and SEM to characterize the effect of precursor concentration on the structural, optical and morphology of ZnONRs. The results are useful in some sense. However, Before I recommend the publication of this work, the manuscript needs significant improvement. Some statements the authors made have no proper explanations. The detailed comments are as followings:
1: At the beginning of the results and discussion part, (starting from page 5 line 43), the authors tried to use XRD to characterize the crystal structures of the samples formed using different precursor concentrations. However, the explanation is not very clear. For example: which border peaks show the formation of ZnO nanostructure (comparing with what peaks)? The authors claimed that the optimum ratio was K0.04 and K0.05 cannot coat the substrate completely. What is the possible reasons for that? Why K0.06 can make the substrate covered completely again according to the XRD (Figure 2) result?

2: In the second paragraph on page 6, the authors said Zn2+ tends to grow on the planar surface of (002). Zinc nitrate hexahydrate and HMT concentrations having a low number of OH-. How can this explain the formation of crystal plane of (002) is limited compared to another plane?
3: In table 1, the errors shown in the average of slopes are very large. How many samples did the authors check using SEM? How many places in one sample did the authors check? What is the uniformity of the samples? It is not convincing to claim the slope has certain trend with the increasing precursor concentration.
4: There are many typos and grammar errors that make the manuscript very difficult to read.

Reviewer #2: In paper entitled "Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration" by M.I.A. Umar, zinc oxide nanorods arrays were obtained through the hydrothermal process at various precursor concentrations under 90˚C for an hour. The effect of precursor concentrations to the structural, optical, and morphology of ZnONRs were studied by using XRD, UV-vis and FESEM. I revise it. The below corrections should do:

1. Authors need to check the English and typo mistakes carefully in the whole manuscript.
2. Why did the authors have chosen ZnONRs as a material for synthesis?
3. What is novelty of this work?
4. Paper has deficiency citation to similar works published before (hydrothermal synthesis). The below references should insert:

* Journal of Alloys and Compounds 625 (2015) 26-33.
* Journal of Alloys and Compounds 617 (2014) 93-101.
* Superlattices and Microstructures 65 (2014) 79-90.
* Mater. Res. Bull. 48 (2013) 3204−3210.
* J. Mater. Sci.: Mater. Electron. 26 (2015) 6831−6836.
* J. Mater. Sci.: Mater. Electron. 27 (2016) 293−303.
* J. Mol. Liq. 220 (2016) 334-338.
* J. Mol. Liq. 219 (2016) 1089−1094.

There is additional documentation related to this decision letter. To access the file(s), please click the link below. You may also login to the system and click the 'View Attachments' link in the Action column.
http://jmse.edmgr.com/l.asp?i=147274&l=1HTC8063

Gmail **Marjoni Imamora <marjoniimamora@gmail.com>**

JMSE-D-17-04705 - Submission Confirmation

1 message

Journal of Materials Science: Materials in Electronics (JMSE) <em@editorialmanager.com>
Tue, Dec 19, 2017 at 12:04 AM
Reply-To: "Journal of Materials Science: Materials in Electronics (JMSE)" <preethi.subramanian@springer.com>
To: Marjoni Imamora <marjoniimamora@gmail.com>

Dear Dr Imamora,

Thank you for submitting your manuscript, Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration, to Journal of Materials Science: Materials in Electronics.

The submission id is: JMSE-D-17-04705
Please refer to this number in any future correspondence.

During the review process, you can keep track of the status of your manuscript by accessing the Editorial Manager web site.

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Should you require any further assistance please feel free to e-mail the Editorial Office by clicking on "Contact Us" in the menu bar at the top of the screen.

With kind regards,
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Gmail **Marjoni Imamora <marjoniimamora@gmail.com>**

Acknowledgement of Receipt of #JMSE-D-17-04705R1

1 message

Journal of Materials Science: Materials in Electronics (JMSE) <em@editorialmanager.com> Sun, Jan 21, 2018 at 1:48 PM
Reply-To: "Journal of Materials Science: Materials in Electronics (JMSE)" <preethi.subramanian@springer.com>
To: Marjoni Imamora <marjoniimamora@gmail.com>

Dear Dr Imamora:

We acknowledge, with thanks, receipt of the revised version of your manuscript, "Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration", submitted to Journal of Materials Science: Materials in Electronics. The manuscript number is JMSE-D-17-04705R1.

You may check the status of your manuscript at any time by accessing the Editorial Manager web site.

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We will inform you of the Editor's decision as soon as possible.

Thank you very much.

Kind regards,
Springer Journals Editorial Office
Journal of Materials Science: Materials in Electronics

Journal of Materials Science: Materials in Electronics

Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration

--Manuscript Draft--

Manuscript Number:	JMSE-D-17-04705R1
Full Title:	Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration
Article Type:	Original Research
Keywords:	Density; precursor concentration, alignment, ZnONRs array
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Order of Authors Secondary Information:	
Funding Information:	The Ministry of Higher Education of Malaysia (MOHE) (03-01-02-SF0836) — Dr Muhammad Mat Salleh
Abstract:	The well-aligned Zinc Oxide Nanorods (ZnONRs) arrays was obtained through the hydrothermal process at various precursor concentrations (PC) under 90˚C for an hour. The effect of PC (0.02, 0.03, 0.04, 0.05, and 0.06M which is denoted as K0.01-K0.06) to the structural, optical, and morfology (diameter, height, slope, and density) of ZnONRs were studied by using X-ray diffraction (XRD), UV-vis spectroscopy, and field emission scanning electron microscopy (FESEM). As-synthesized ZnONRs have uniform growth directions along the [002] orientations with average diameters in the range of 40-90 nm. These nanorods showed a strong optical absorption peak up to 367 nm which is suitable for gap energy of ZnO 3.37 eV indicated that the formation of ZnONRs. The morfology of ZnONRs in term of diameter, height, slope, and density increases with the PC. The highest of the density of 182 number/μm-2 with average slope of 6 degree (aligned percentage of 83 ± 12 %) was obtained at the PC of K0.04. It is interesting to find that the dye sensitized solar cell of K0.04 with showed 5 times increase in power conversion efficiency as compared to that with PC of K0.02.

21 January 2018

Dear Editor,

SUBMISSION OF A REVISED MANUSCRIPT FOR EVALUATION

Thank you for the opportunity to revise our manuscript. We would like to submit the revised version of our manuscript entitled “"Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration" (REF: #JMSE-D-17-04705) to the Journal of Materials Science: Materials in Electronics.

We have considered for almost of comment and suggestion of the reviewer and give a few arguments for certain comments and suggestions of the reviewer. We agreed with the comments and corrections of reviewer. We thank the Editor and the reviewer for their detailed and thoughtful critiques. Below we summarize our point-by-point responses to the reviewer’s comments. We believe that all of the comments have been addressed in a way that the reviewer would find satisfactory.

Reviewer#1: 1) At the beginning of the results and discussion part, (starting from page 5 line 43), the authors tried to use XRD to characterize the crystal structures of the samples formed using different precursor concentrations. However, the explanation is not very clear. For example: which border peaks show the formation of ZnO nanostructure (comparing with what peaks)?

‘’.., which border peaks show the formation of ZnO nanostructure’’ has been change in the revised paper with ‘This reflects that this crystal plane mainly oriented parallel to the substrate, rendering the nanorod growth are oriented on that plane, which is in good agreement with the previous report [2, 27].’’

The authors claimed that the optimum ratio was K0.04 and K0.05 cannot coat the substrate completely. What is the possible reason for that? Why K0.06 can make the substrate covered completely again according to the XRD (Figure 2) result?

In the revised paper has been added the reasons related the reviewer question, as follows:

‘’At high concentrations, the formed Zn2+ and OH- ions are believed to dominantly promote to the growth of growing ZnONRs, instead of promoting others nanoseed on the substrate surface. As a result, there is some area of substrate that is not coverage by ZnONRs. When excessive PC concentration is further available in the reaction, for example in the case of sample K0.06, the formed zinc and hydroxyl ions, beside promoting the nanorod’s height growth they also accelerate the lateral growth of the nanorods, producing larger diameter nanorod on the surface [29]. Owing to the availability of un-coverage surface, lower X-ray diffraction intensity from this plane is expected.’’

2: In the second paragraph on page 6, the authors said Zn^{2+} tends to grow on the planar surface of (002). Zinc nitrate hexahydrate and HMT concentrations having a low number of OH-. How can this explain the formation of crystal plane of (002) is limited compared to another plane?

The above statement has been change in the revised paper with '' During ZnONRs growth process, there are two major components that play an important role i.e. zinc nitrate hexahydrate and hexamethylenetetramine (HMT), which form tetrahedral [Zn(OH)4]-2or [Zn(NH3)]+2 complexes [30, 31]. This complex will be hydrolized forming chemically un-stable ZnO4 complex, which then will be dissociated, promoting the growth of ZnO nanocrystals. In the presence of unique polymorphism of hexagonal wurtzite structure [32, 33], the nanocrystal growth of ZnO oxide will possess dominant (002) crystal plane [29].

3: In table 1, the errors shown in the average of slopes are very large. How many samples did the authors check using SEM? How many places in one sample did the authors check? What is the uniformity of the samples? It is not convincing to claim the slope has certain trend with the increasing precursor concentration.

The average slope data in the table 1 has been changed in the revised paper.

4: There are many typos and grammar errors that make the manuscript very difficult to read.

The Typos and grammar errors has been corrected in the revised paper.

Reviewer #2: 1. Authors need to check the English and typo mistakes carefully in the whole manuscript.

The Typos and grammar errors has been corrected in the revised paper.

2. Why did the authors have chosen ZnONRs as a material for synthesis?

The reasons has been added in the revised paper

3. What is novelty of this work?

The novelty of this work is the discovery of optimum parameters, especially PC to produce the well-aligned and compact of ZnONRs which to be applied into DSSC and nanogenerator application.

4. Paper has deficiency citation to similar works published before (hydrothermal synthesis). The below references should insert:

* Journal of Alloys and Compounds 625 (2015) 26-33.

* Journal of Alloys and Compounds 617 (2014) 93-101.

* Superlattices and Microstructures 65 (2014) 79-90.

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* J. Mater. Sci.: Mater. Electron. 27 (2016) 293−303.

* J. Mol. Liq. 220 (2016) 334-338.

* J. Mol. Liq. 219 (2016) 1089−1094.

The above papers have been referenced in the revised paper.

Thank you very much for your co-operation.

Sincerely,

Dr. Marjoni Imamora

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*Marked Manuscript

Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering uponPrecursor Concentration

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Akrajas Ali Umar[2].

[1] Department of Physics Education, Faculty of Tarbiyah and Teaching, Institut Agama Islam Negeri (IAIN) Batusangkar, 27213, West Sumatera, Indonesia

[2] Institute of Microengineering and Nanoelectronics (IMEN), UniversitiKebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

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Abstract

The well-aligned Zinc Oxide Nanorods (ZnONRs) arrays was obtained through a hydrothermal process at various precursor concentrations (PC)under a growth temperature of 90˚C for an hour. The effect of PC (0.02, 0.03, 0.04, 0.05, and 0.06M which is denoted as K0.01-K0.06) tothe structural, optical, and morfology (diameter, height, slope, and density) of ZnONRs were studied by using X-ray diffraction (XRD), UV–vis spectroscopy, and field emission scanning electron microscopy (FESEM). As-synthesized ZnONRs exhibit an uniform growth direction along the [002] orientations with average diameters in the range of 40–90 nm. These nanorods showed a strong optical absorption peak centering at 367 nm,which is equivalent to optical energy band gap of ZnO 3.37 eV, confirming the formation of ZnONRs. The morfology of ZnONRs in term of diameter, height, slope, and density increases with the PC. The highest density of approximately 182 number/μm^{-2} with average slope of 6 degree (aligning percentage of 83 ± 12 %) was obtained at the PC of K0.04. It is interesting to find that the dye sensitized solar cell utilizing the sample K0.04 showed 5 times increasing in the power conversion efficiency as compared to that of device utilizing K0.02 sample.

Keyword: density; precursor concentration, alignment, ZnONRs array

1. Introduction

Research efforts to produce an extended and well-align of ZnOnanorods (ZnONRs) has been obtaining a continuous attention in the last few decades due to their unique electrical and optical properties[1]. Besides that, the ZnONRs is expected to further enhance their intrinsic property and make them as a potential material candidates for many applications, such as chemical and biology sensor, microelectronics devices, energy conversion and storage [2]. Previously, Tian and his co-worker have been successfully preparing the aligned ZnONRs by using a high-temperature vacuum deposition[3]. However, it usually requires a single-crystal substrate and applied in a high operating temperature, inferring it is an expensive method [4]. In addition, this method is inappropriate for organics substrate for a microelectronic application. Similarly, Singh and his co-worker also report a facile method to produce well-aligned ZnONRs via a controlled thermal evaporation of Zn powder [5]. However, it also requires a high preparation's temperature and gas application (argon and oxygen) during the preparation process.

Recently, many approaches for preparing ZnONRs on the surface of the organic substrate at low temperature has been introduced and widely used. Such as through anodic aluminium oxide template electrochemical, and hydrothermal methods [6-14]. Among the available techniques, the hydrothermal methods is a very suitable to produce ZnONRs with high-density and well-aligned under a low temperature processing [6]. Since the property of ZnONRs, such as morphologies, compositions, and alignment, strongly depend on the synthesis protocol, particularly the precursor concentration, to control the synthetic condition may produce well-aligned ZNONRs on substrate surface. In this paper, we demonstrate the preparation of well-aligned ZnONRs by controlling the concentration of precursors (PC) during the growth process. A suitable condition that project the growth of high-density and well-aligned ZnONRs are obtained. The synthetic method and the mechanism for the growth of high-density and well-aligned ZnONRs will be discussed.

2. Experimental

In a typical procedure, we grouped the study into two simple steps, namely: preparation of ZnONRs, and fabrication a photovoltaic electrochemical cell. The detailed of each step will be explained as follows:

2.1. Preparation of ZnONRs

ZnONRs arrays were prepared on FTO on glass substrates which were pre-coated with ZnO nanoparticles seed using hydrothermal process. ZnO nanoparticles seeds were prepared by a sol-gel process using a reaction containing zinc acetate (Zn $(H_3COO)_2.H2O$) (98%, Sigma-Aldrich) and DEA ($C_4H_{11}NO_2$) (99%, Sigma-Aldrich) in ethanol. Thin film of ZnO nanoparticles seeds on FTO substrate were then prepared by a spin-coating method at 400 rpm for 30 s. The FTO substrate containing the ZnO nanoparticles seed was then subjected to an annealing process at 300^{o}C in air for an hour. The ZnONRs were grown up from the nanoparticles seed via a hydrothermal method in a growth solution containing equimolar zinc nitrate hexahydrate (99%, Sigma-Aldrich) and hexamethyl-tetramine (99%, Sigma-Aldrich) in DI water. The reaction was then carried out in an auto-clave at 90°C for 1h. The detail of the ZnONRs preparation processes has been described elsewhere [15-17]. In this paper, the growth solution concentration was varied from 0.02-0.06 M with sample's name denoted as K0.02, K0.03, K0.04, K0.05, and K0.06. All chemical reagents used in the experiment are of analytical grade and used without further purification.

2.2. Fabrication of Photovoltaic Electrochemical Cell

The preparation of ZnONRs as the photovoltaic material has been described in the previous section. Platinum [18-21] have been used as a counter electrode to study the photovoltaic performance of dye-sensitized solar cell (DSSC). Platinum is prepared by using

magnetron sputtering technique by using platinum pellet on FTO substrate at 2.5 kV for 2 minutes under vacuum. An electrolyte containing a redox couple of iodide/tri-iodide, i.e. a mixture of 0.5 M LiI,0.05 M I_2 and 0.5 M tertbutyl pyridine in acetonitrile was used in this study [19, 20, 22-26]. The electrolyte was sandwiched between the ZnONRs structure and platinum as a counter electrode as shown in Fig.1. The resultant cell was clamped each other using a paper clip and the photovoltaic performance of DSSC cell was studied by using an AM 1.5 simulated sun light with an intensity of 100 $mWcm^{-2}$. The current density (J)–voltage (V) curve of cell underactive area of 0.23 $cm^2$was recorded by using Gamry 1000 interface measurement unit. Meanwhile, the X-Ray diffraction (XRD), Halo DB-20 UV-Vis spectrometer, and Carl Zeiss Supra 55VP field emission scanning electron microscopy (FESEM) were used to investigate the composite structure, optical absorbance properties, and morphology of the sample.

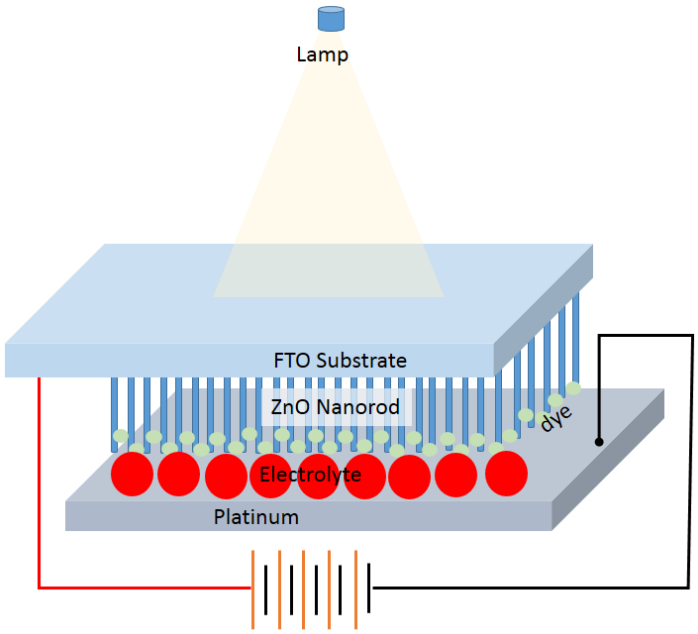


Fig. 1. The DSSC cell with ZnONRs/Electrolyte/Platinum structure

3. Result and discussion

The crystal structures of the samples were characterized using Bruker D8 Advanced X-ray diffractometer with CuKα irradiation operated at a scan rate of 0.025 ◦/0.1 s. The XRD spectra of the nanorod grown using various precursor concentrations (K0.02, K0.03, K0.04, K0.05, and K0.06) are shown in Fig.2. There are four XRD peaks detected from the sample,of which can be associated with the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451) with the diffraction peaks at position of 2θ = 31.9°, 34.4°, 36.48 ° and 2θ = 47.75° correspond to the diffraction from the crystal plane of (100), (002), (101) and (102), respectively. As can be seen from the figure, the diffraction intensity from the crystalline plane of (002) is much higher compared to others crystal plane. This reflects that this crystal plane mainly oriented parallel to the substrate, rendering the nanorod growth are oriented on that plane, which is in good agreement with the previous report [2, 27]. Thus, the crystal plane of (002) is oriented perpendicular to the direction of the c-axis [28]. In addition, in the sample of K0.02, K0.03 and K0.05, it is also detected a weak peak at 2θ = 38°, which is believed to be from the FTO substrate. The second highest diffraction peaks is from the crystal plane of (101). The ratio of the peak height of the plane (002) to the plane (101) increase as the PC increased. The optimum ratio was achieved on the sample of K0.04. However, the ratio decreases when the PC concentration further augmented (K0.05) due to low-density of nanorod growth as the result of high steric hindrance at high PC concentration.

At high concentrations, the formed Zn^{2+} and OH^{-} ions are believed to dominantly promote to the growth of growing ZnONRs, instead of promoting others nanoseed on the substrate surface. As a result, there is some area of substrate that is not coverage by ZnONRs.

When excessive PC concentration is further available in the reaction, for example in the case of sample K0.06, the formed zinc and hydroxyl ions, beside promoting the nanorod's height growth they also accelerate the lateral growth of the nanorods, producing larger diameter nanorod on the surface[29]. Owing to the availability of un-coverage surface, lower X-ray diffraction intensity from this plane is expected.

During ZnONRs growth proces, there are two major components that play an important role i.e. zinc nitrate hexahydrate and hexamethylenetetramine (HMT), which form tetrahedral $[Zn(OH)_4]^{-2}$or $[Zn(NH_3)]^{+2}$ complexes [30, 31]. This complex will be hydrolized forming chemically un-stable ZnO_4 complex, which then will be dissociated, promoting the growth of ZnO nanocrystals. In the presence of unique polymorphism of hexagonal wurtzite structure [32, 33], the nanocrystal growth of ZnO oxide will possess dominant (002) crystal plane [29].

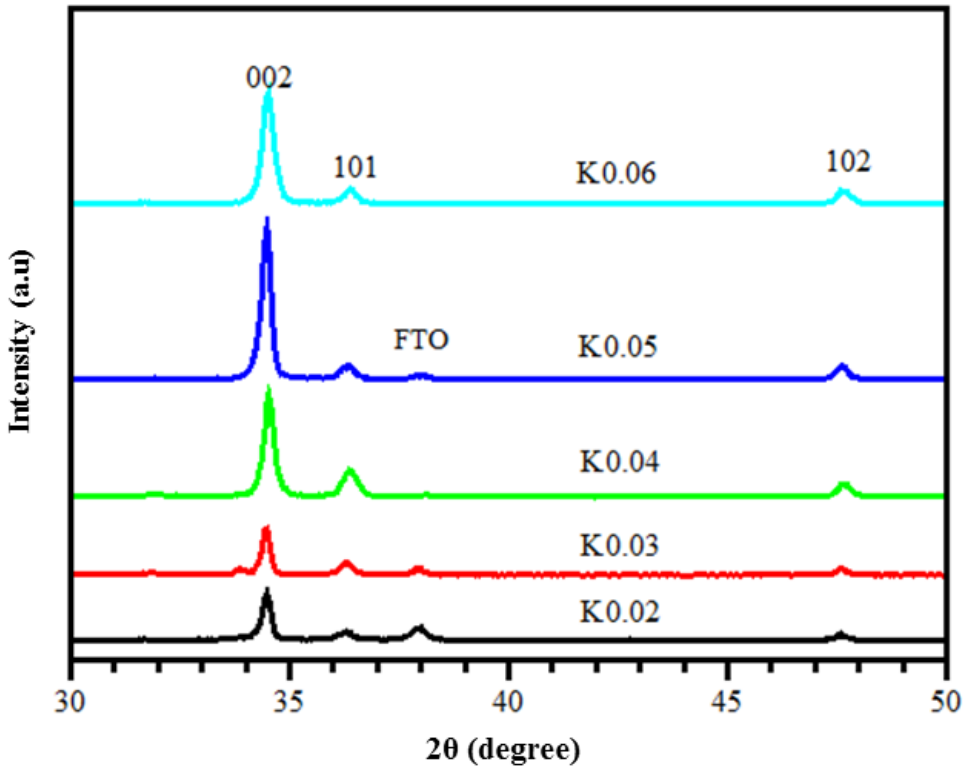


Fig.2. The XRD spectra of ZnONRs at various condition of PC.

The morphology of ZnONRs grown on the FTO substrate that are prepared using various PC are examined using FESEM analysis (see Fig 3). As the Figure 3a reveals, for the samples prepared at low PC (K0.02), it can be seen that the average diameter and height of ZnONRs is 43 and 283 nm, respectively. Meanwhile the average growth's orientation of the rod normal to the substrate surface is 10.9°. This shows that the ZnONRs growth for this PC is somewhat rare and still have the surface,which is not overgrown by nanorod. Due to such condition, the ZnONRsgrowth seems skewed with the average density of 136 rod/μm^2.

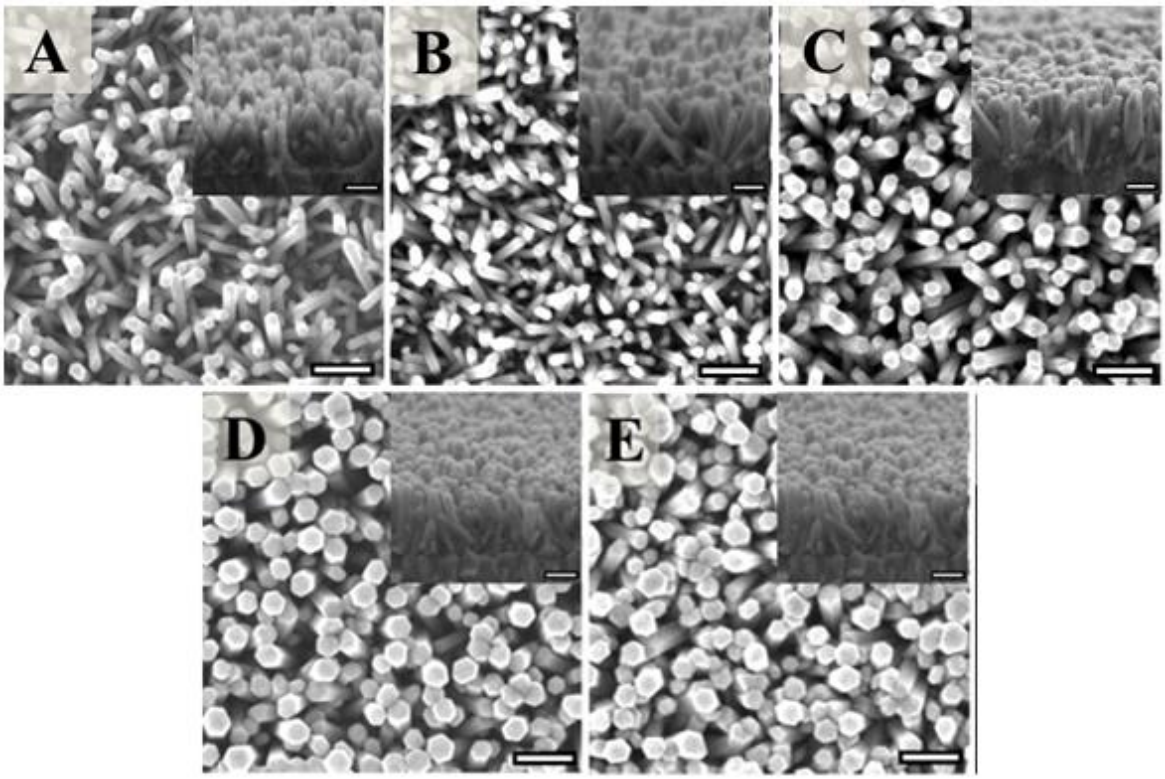


Fig.3. (A-E) are the FESEM image of ZnONRs grown at various concentration of PC, i.e. 0.02-0.06M. The *inset* figure is the cross-sectional image of corresponding ZnONRs.

By increasing the PC (see Fig 3b, 3c, and 3d), the diameter and height of ZnONRs increased. While the average slope decreased with the increasing of PC and maximum at sample K0.05 (see Table 1). This could be due to the increasing of the diameter of nanorods, resulting in the enhancement of inter-rods coupling supporting well-vertical aligned ZnONRs growth on the substrate. At high of PC, i.e. samples of K0.05 and K0.06 (see Fig 3d, and 3e), most of the nanorod diameter are higher than 100 nm. Therefore, considering the nanoregime is in between of 1-100 nm, the optimum PC for well-aligned ZnONRs growth is K0.04.

Futhermore, the nanorod density,which is determined by the number of nanorod growth over the substrate area, shows increasing with the increasing of PC and optimum on the sample K0.04. When the PC further augmented, the density significantly decrease as the result of nanorod diameter increasing. From the Table 1, it can be seen that that (based on the diameter, height, slopeand density)the well-aligned ZnONRs was achieved at the sample of K0.04. This is in good agreement with the XRD results.

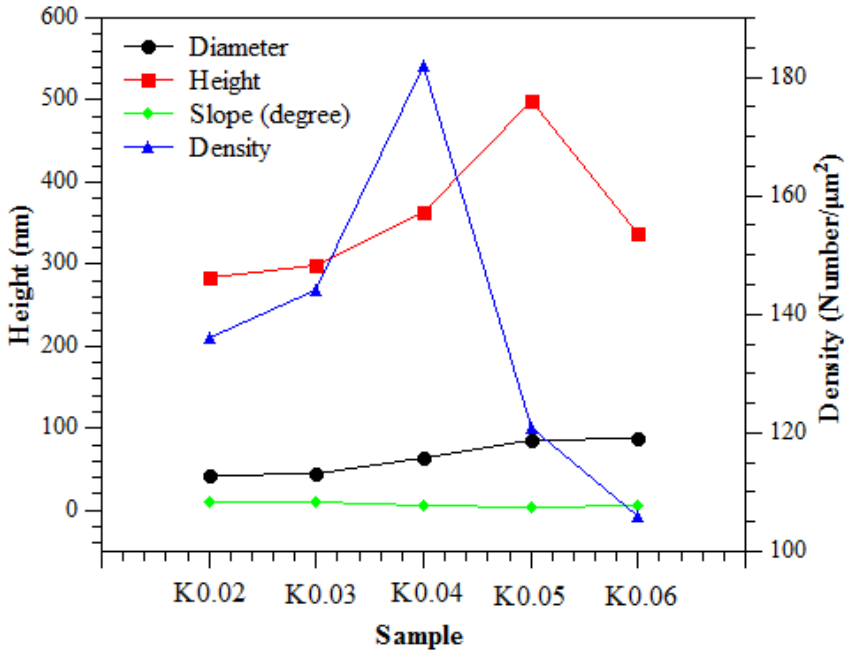
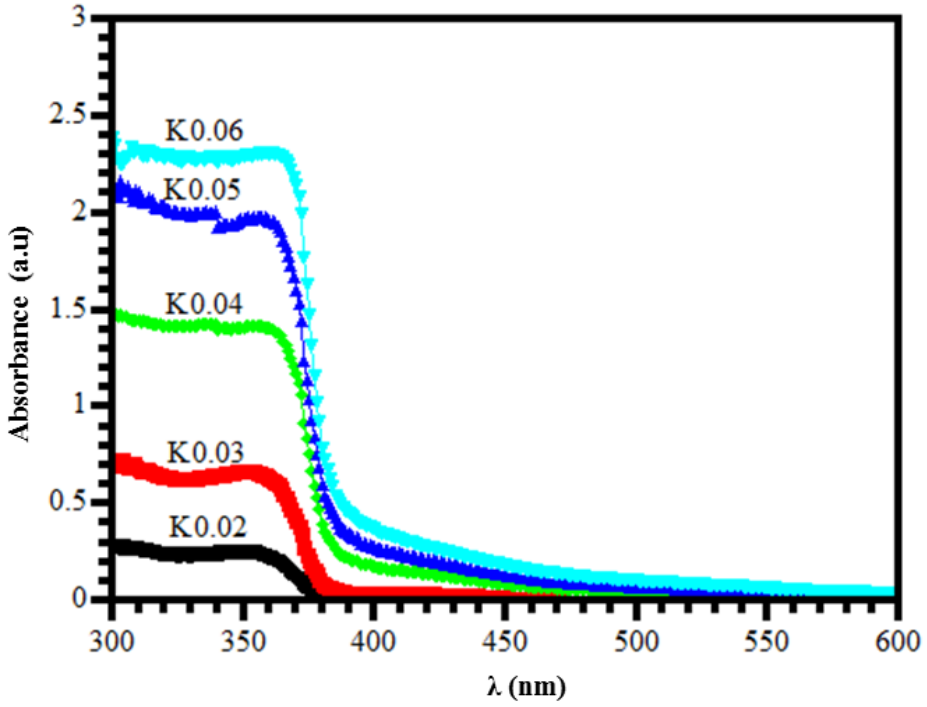


Fig.4. The diameter, height, slope and density of ZnONRs at various PC condition (K0.02-K0.06).

Table1.The diameter, height, slope, and densitydata of ZnONRs at various PC

Sample	The average of diameter (nm)	The average of height (nm)	The Average of slope (degree)	Density (Number/ μm^2)
K0.02	43.47 ± 4.7	283.27 ± 47	10.9 ± 1.5	136
K0.03	44.44 ± 5.5	298.18 ± 49	9.7 ± 1.4	144
K0.04	64.14 ± 8.3	363.72 ± 34	6.0 ± 1.0	182
K0.05	86.50 ± 9.8	498.72± 116	3.4 ± 2.2	121
K0.06	87.82 ± 7.5	336.81 ±41	6.8 ± 1.1	106

The optical absorption properties of ZnONRs was examined via UV-VIS spectroscopy in the wavelength range of 300-600 nm (see Fig. 4). From the figure it can be seen that the entire samples of ZnONRs exhibit an absorption band centering at 367 nm. This is equivalent to optical band gap energy of ZnO, i.e. 3.37 eV. it can also be seen that the absorbance of the sample increases with the increasing of PC. This is due to the increasing in the diameter and height of the nanorod as well as the surface area [34]. This condition would be beneficial for adsorption of much dye when being used as photoanode of DSSC, improving the power conversion efficiency (PCE) [35, 36].



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This is presumably attributed to the loss in the quantum effect as the ZnONRs size are larger than 100 nm.

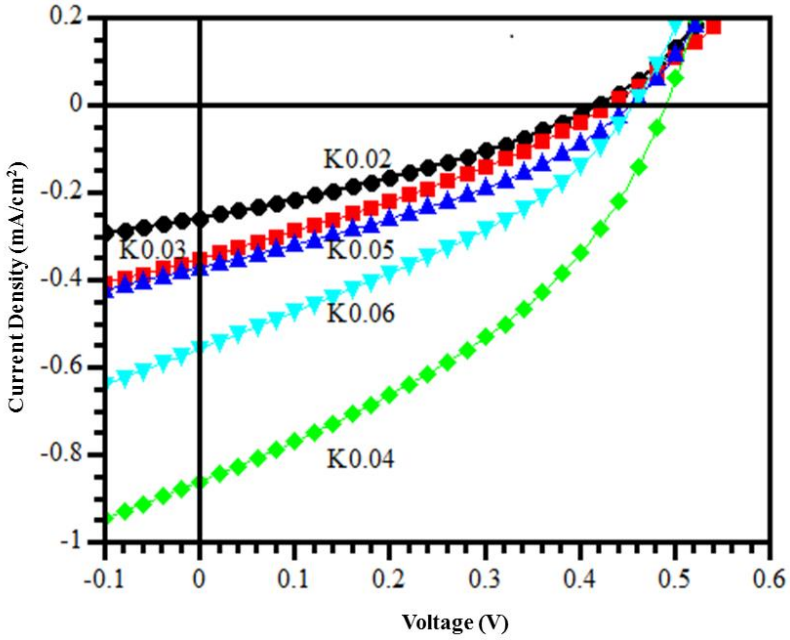

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Table 2 The photovoltaic parameter of the DSSCs devices.

Sampel	Voc (V)	Jsc (mA/cm^2)	PCE (%)	FF (%)
K0.02	0.42	0.26	0.03	0.32
K0.03	0.43	0.36	0.05	0.30
K0.04	0.49	0.86	0.16	0.38
K0.05	0.45	0.37	0.06	0.34
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The well-aligned ZnONRs arrays on substrate surface has been sucessfully obtained via a hydrothermal process at various PC under 90˚C for an hour of growth time. The red shifts of the

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Acknowledgment

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*Revised Manuscript

Hydrothermally Grown of Well-Aligned ZnONRs: Dependence of Alignment Ordering upon Precursor Concentration

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Abstract

The well-aligned Zinc Oxide Nanorods (ZnONRs) arrays was obtained through a hydrothermal process at various precursor concentrations (PC)under a growth temperature of 90˚C for an hour. The effect of PC (0.02, 0.03, 0.04, 0.05, and 0.06M which is denoted as K0.01-K0.06) tothe structural, optical, and morfology (diameter, height, slope, and density) of ZnONRs were studied by using X-ray diffraction (XRD), UV–vis spectroscopy, and field emission scanning electron microscopy (FESEM). As-synthesized ZnONRs exhibit an uniform growth direction along the [002] orientations with average diameters in the range of 40–90 nm. These nanorods showed a strong optical absorption peak centering at 367 nm,which is equivalent to optical energy band gap of ZnO 3.37 eV, confirming the formation of ZnONRs. The morfology of ZnONRs in term of diameter, height, slope, and density increases with the PC. The highest density of approximately 182 number/μm^{-2} with average slope of 6 degree (aligning percentage of 83 ± 12 %) was obtained at the PC of K0.04. It is interesting to find that the dye sensitized solar cell utilizing the sample K0.04 showed 5 times increasing in the power conversion efficiency as compared to that of device utilizing K0.02 sample.

Keyword: density; precursor concentration, alignment, ZnONRs array

1. Introduction

Research efforts to produce an extended and well-align of ZnO nanorods (ZnONRs) has been obtaining a continuous attention in the last few decades due to their unique electrical and optical properties[1]. Besides that, the ZnONRs is expected to further enhance their intrinsic property and make them as a potential material candidates for many applications, such as chemical and biology sensor, microelectronics devices, energy conversion and storage [2]. Previously, Tian and his co-worker have been successfully preparing the aligned ZnONRs by using a high-temperature vacuum deposition [3]. However, it usually requires a single-crystal substrate and applied in a high operating temperature, inferring it is an expensive method [4]. In addition, this method is inappropriate for organics substrate for a microelectronic application. Similarly, Singh and his co-worker also report a facile method to produce well-aligned ZnONRs via a controlled thermal evaporation of Zn powder [5]. However, it also requires a high preparation's temperature and gas application (argon and oxygen) during the preparation process.

Recently, many approaches for preparing ZnONRs on the surface of the organic substrate at low temperature has been introduced and widely used. Such as through anodic aluminium oxide template electrochemical, and hydrothermal methods [6-14]. Among the available techniques, the hydrothermal methods is a very suitable to produce ZnONRs with high-density and well-aligned under a low temperature processing [6]. Since the property of ZnONRs, such as morphologies, compositions, and alignment, strongly depend on the synthesis protocol, particularly the precursor concentration, to control the synthetic condition may produce well-aligned ZNONRs on substrate surface. In this paper, we demonstrate the preparation of well-aligned ZnONRs by controlling the concentration of precursors during the growth process. A suitable condition that project the growth of high-density and well-aligned ZnONRs are obtained. The synthetic method and the mechanism for the growth of high-density and well-aligned ZnONRs will be discussed.

2. Experimental

In a typical procedure, we grouped the study into two simple steps, namely: preparation of ZnONRs, and fabrication a photovoltaic electrochemical cell. The detailed of each step will be explained as follows:

2.1. Preparation of ZnONRs

ZnONRs arrays were prepared on FTO on glass substrates which were pre-coated with ZnO nanoparticles seed using hydrothermal process. ZnO nanoparticles seeds were prepared by a sol-gel process using a reaction containing zinc acetate ($Zn(H_3COO)_2.H2O$) (98%, Sigma-Aldrich) and DEA ($C_4H_{11}NO_2$) (99%, Sigma-Aldrich) in ethanol. Thin film of ZnO nanoparticles seeds on FTO substrate were then prepared by a spin-coating method at 400 rpm for 30 s. The FTO substrate containing the ZnO nanoparticles seed was then subjected to an annealing process at 300^{o}C in air for an hour. The ZnONRs were grown up from the nanoparticles seed via a hydrothermal method in a growth solution containing equimolar zinc nitrate hexahydrate (99%, Sigma-Aldrich) and hexamethyl-tetramine (99%, Sigma-Aldrich) in DI water. The reaction was then carried out in an auto-clave at 90°C for 1h. The detail of the ZnONRs preparation processes has been described elsewhere [15-17]. In this paper, the growth precursor concentration (PC) was varied from 0.02-0.06 M with sample's name denoted as K0.02, K0.03, K0.04, K0.05, and K0.06. All chemical reagents used in the experiment are of analytical grade and used without further purification.

2.2. Fabrication of Photovoltaic Electrochemical Cell

The preparation of ZnONRs as the photovoltaic material has been described in the previous section. Platinum [18-21] have been used as a counter electrode to study the photovoltaic performance of dye-sensitized solar cell (DSSC). Platinum is prepared by using

magnetron sputtering technique by using platinum pellet on FTO substrate at 2.5 kV for 2 minutes under vacuum. An electrolyte containing a redox couple of iodide/tri-iodide, i.e. a mixture of 0.5 M LiI,0.05 M I_2 and 0.5 M tertbutyl pyridine in acetonitrile was used in this study [19, 20, 22-26]. The electrolyte was sandwiched between the ZnONRs structure and platinum as a counter electrode as shown in Fig.1. The resultant cell was clamped each other using a paper clip and the photovoltaic performance of DSSC cell was studied by using an AM 1.5 simulated sun light with an intensity of 100 $mWcm^{-2}$. The current density (J)–voltage (V) curve of cell underactive area of 0.23 $cm^2$was recorded by using Gamry 1000 interface measurement unit. Meanwhile, the X-Ray diffraction (XRD), Halo DB-20 UV-Vis spectrometer, and Carl Zeiss Supra 55VP field emission scanning electron microscopy (FESEM) were used to investigate the composite structure, optical absorbance properties, and morphology of the sample.

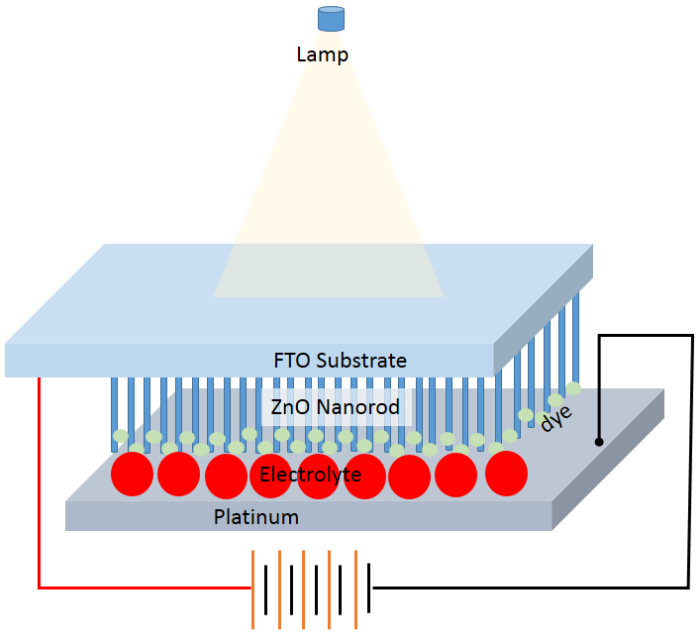


Fig. 1. The DSSC cell with ZnONRs/Electrolyte/Platinum structure

3. Result and discussion

The crystal structures of the samples were characterized using Bruker D8 Advanced X-ray diffractometer with CuKα irradiation operated at a scan rate of 0.025 ◦/0.1 s. The XRD spectra of the nanorod grown using various precursor concentrations (K0.02, K0.03, K0.04, K0.05, and K0.06) are shown in Fig.2. There are four XRD peaks detected from the sample,of which can be associated with the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451) with the diffraction peaks at position of 2θ = 31.9°, 34.4°, 36.48 ° and 2θ = 47.75° correspond to the diffraction from the crystal plane of (100), (002), (101) and (102), respectively. As can be seen from the figure, the diffraction intensity from the crystalline plane of (002) is much higher compared to others crystal plane. This reflects thatthis crystal plane mainly oriented parallel to the substrate, rendering the nanorod growth are oriented on that plane, which is in good agreement with the previous report [2, 27]. Thus, the crystal plane of (002) is oriented perpendicular to the direction of the c-axis [28]. In addition, in the sample of K0.02, K0.03 and K0.05, it is also detected a weak peak at 2θ = 38°, which is believed to be from the FTO substrate. The second highest diffraction peaks is from the crystal plane of (101). The ratio of the peak height of the plane (002) to the plane (101) increase as the PC increased. The optimum ratio was achieved on the sample of K0.04. However, the ratio decreases when the PC concentration further augmented (K0.05) due to low-density of nanorod growth as the result of high steric hindrance at high PC concentration.

At high concentrations, the formed Zn^{2+} and OH^- ions are believed to dominantly promote to the growth of growing ZnONRs, instead of promoting others nanoseed on the substrate surface. As a result, there is some area of substrate that is not coverage by ZnONRs.

When excessive PC concentration is further available in the reaction, for example in the case of sample K0.06, the formed zinc and hydroxyl ions, beside promoting the nanorod's height growth they also accelerate the lateral growth of the nanorods, producing larger diameter nanorod on the surface[29]. Owing to the availability of un-coverage surface, lower X-ray diffraction intensity from this plane is expected.

During ZnONRs growth proces, there are two major components that play an important role i.e. zinc nitrate hexahydrate and hexamethylenetetramine (HMT), which form tetrahedral $[Zn(OH)_4]^{-2}$or $[Zn(NH_3)]^{+2}$ complexes [30, 31]. This complex will be hydrolized forming chemically un-stable ZnO_4complex, which then will be dissociated,promoting the growth of ZnO nanocrystals. In the presence of unique polymorphism of hexagonal wurtzite structure [32, 33], the nanocrystal growth of ZnO oxide will possess dominant (002) crystal plane [29].

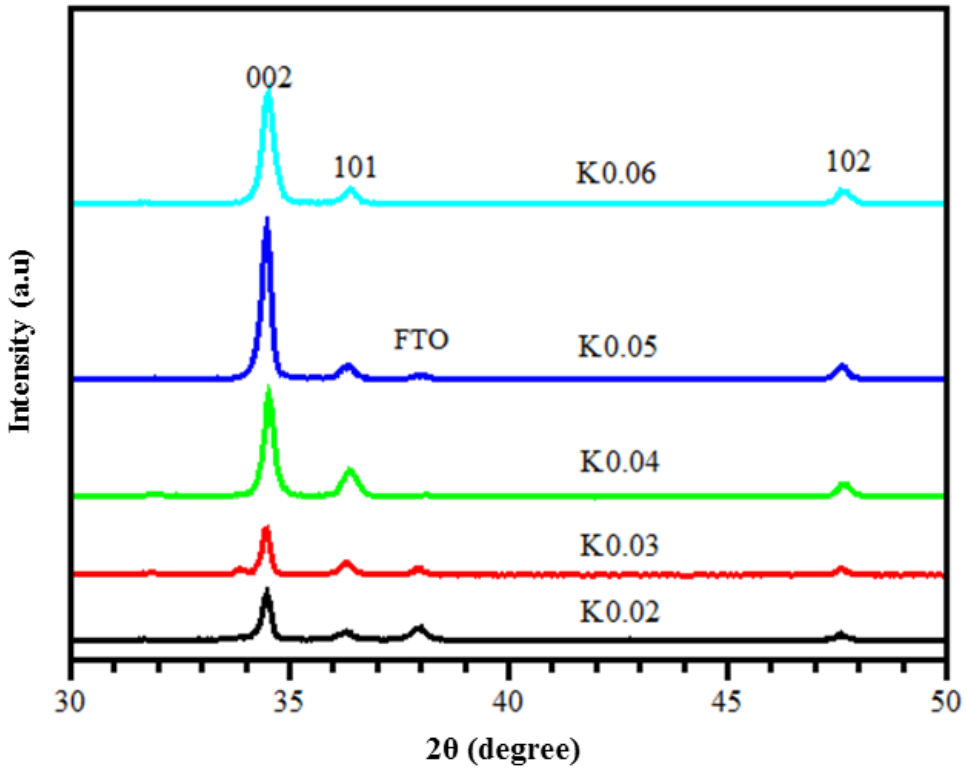


Fig.2. The XRD spectra of ZnONRs at various condition of PC.

The morphology of ZnONRs grown on the FTO substrate that are prepared using various PC are examined using FESEM analysis (see Fig 3). As the Figure 3a reveals, for the samples prepared at low PC (K0.02), it can be seen that the average diameter and height of ZnONRs is 43 and 283 nm, respectively. Meanwhile the average growth's orientation of the rod normal to the substrate surface is 10.9°. This shows that the ZnONRs growth for this PC is somewhat rare and still have the surface,which is not overgrown by nanorod. Due to such condition, the ZnONRsgrowth seems skewed with the average density of 136 rod/μm^2.

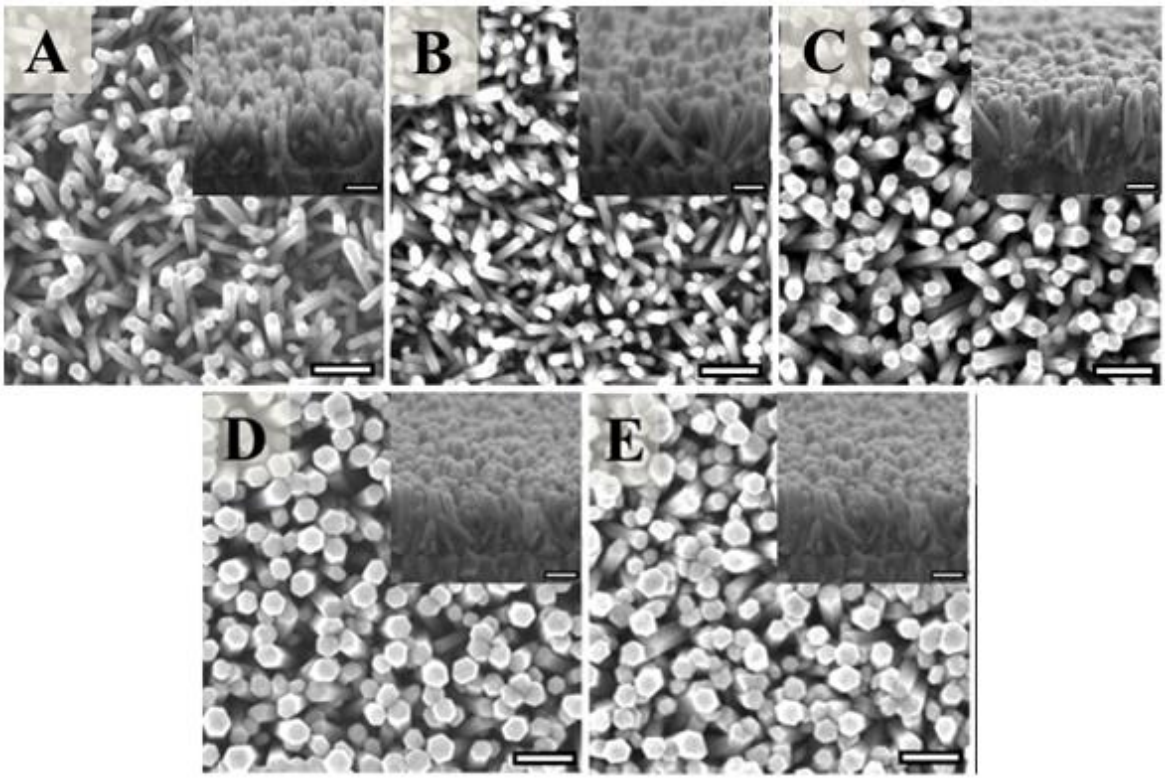


Fig.3. (A-E) are the FESEM image of ZnONRs grown at various concentration of PC, i.e. 0.02-0.06M. The *inset* figure is the cross-sectional image of corresponding ZnONRs.

By increasing the PC (see Fig 3b, 3c, and 3d), the diameter and height of ZnONRs increased. While the average slope decreased with the increasing of PC and maximum at sample K0.05 (see Table 1). This could be due to the increasing of the diameter of nanorods, resulting in the enhancement of inter-rods coupling supporting well-vertical aligned ZnONRs growth on the substrate. At high of PC, i.e. samples of K0.05 and K0.06 (see Fig 3d, and 3e), most of the nanorod diameter are higher than 100 nm. Therefore, considering the nanoregime is in between of 1-100 nm, the optimum PC for well-aligned ZnONRs growth is K0.04.

Futhermore, the nanorod density,which is determined by the number of nanorod growth over the substrate area, shows increasing with the increasing of PC and optimum on the sample K0.04. When the PC further augmented, the density significantly decrease as the result of nanorod diameter increasing. From the Table 1, it can be seen that that (based on the diameter, height, slopeand density)the well-aligned ZnONRs was achieved at the sample of K0.04. This is in good agreement with the XRD results.

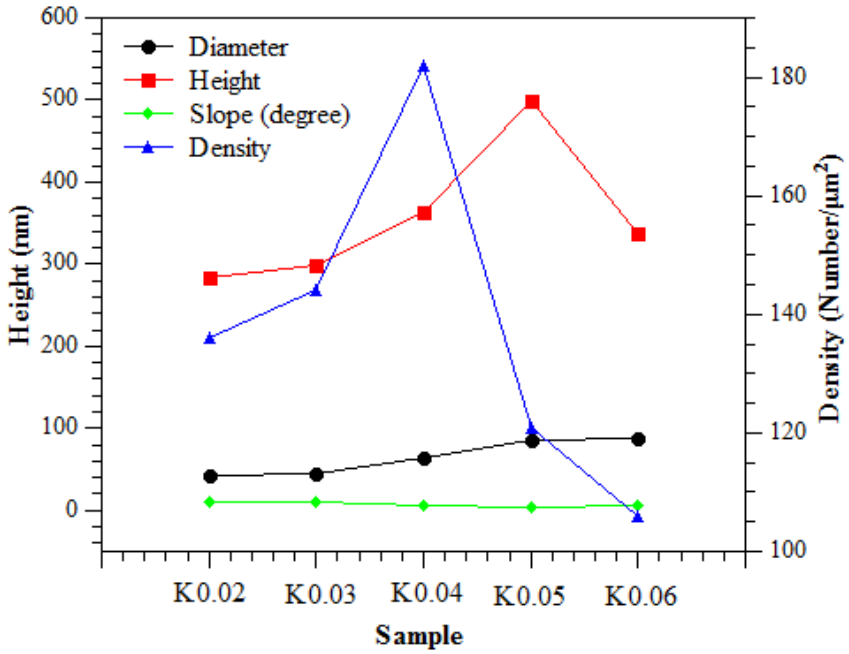
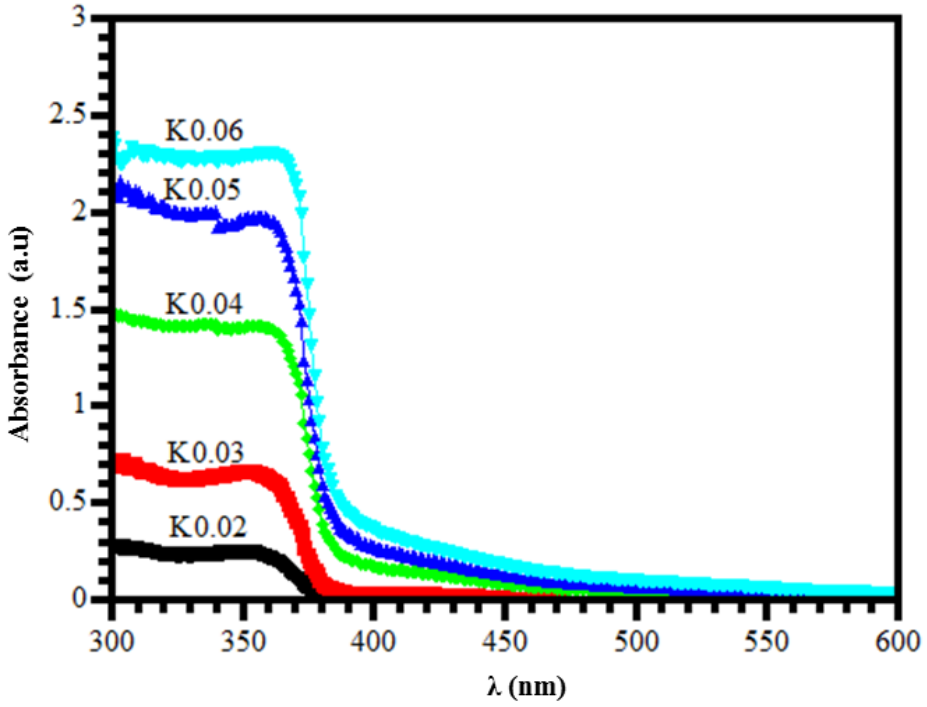


Fig.4. The diameter, height, slope and density of ZnONRs at various PC condition (K0.02-K0.06).

Table2.The diameter, height, slope, and densitydata of ZnONRs at various PC

Sample	The average of diameter (nm)	The average of height (nm)	The Average of slope (degree)	Density (Number/ μm^2)
K0.02	43.47 ± 4.7	283.27 ± 47	10.9 ± 1.5	136
K0.03	44.44 ± 5.5	298.18 ± 49	9.7 ± 1.4	144
K0.04	64.14 ± 8.3	363.72 ± 34	6.0 ± 1.0	182
K0.05	86.50 ± 9.8	498.72± 116	3.4 ± 2.2	121
K0.06	87.82 ± 7.5	336.81 ±41	6.8 ± 1.1	106

The optical absorption properties of ZnONRs was examined via UV-VIS spectroscopy in the wavelength range of 300-600 nm (see Fig. 4). From the figure it can be seen that the entire samples of ZnONRs exhibit an absorption band centering at 367 nm. This is equivalent to optical band gap energy of ZnO, i.e. 3.37 eV. it can also be seen that the absorbance of the sample increases with the increasing of PC. This is due to the increasing in the diameter and height of the nanorod as well as the surface area [34]. This condition would be beneficial for adsorption of much dye when being used as photoanode of DSSC, improving the power conversion efficiency (PCE) [35, 36].



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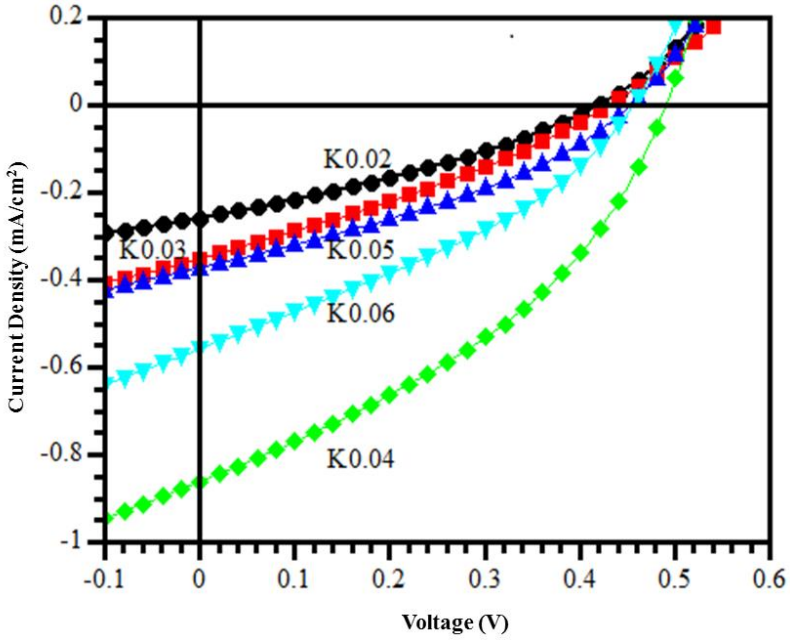

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The well-aligned ZnONRs arrays on substrate surface has been sucessfully obtained via a hydrothermal process at various PC under 90˚C for an hour of growth time. The red shifts of the

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