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Nano-rods oxide materials for biosensor application

H. A. Wahab[1],I. K. Battisha[1], A.A. El Saeid[2] and A. A. Salama[2]
[1]Solid State Physics Department, Physics Division, National Research Center (NRC), 33 Bohouth St, Dokki, Giza, [2] Physics Department, El Azhar University, Cairo, Egypt

IRON ions selective biosensor (Fe^{3+}) based on zinc oxide nano-rods thin film symbolic as ZnO-(NRs)TF was develop and prepared. $FeCl_3$ solutions with concentration ranging from 10^{-6} M up to 10^{-2} Mused for studied the Fe^{3+} ions potentiometric response by usedZnO-(NRs)TF deposited on conducting plastic and silicon substrates as working electrodes versus reference electrode (Ag/AgCl). TheZnO-(NRs)TF was grown on conducting plastic and silicon substrates by used two methods (Sol - Gel and aqueous chemical growth (ACG)) as seed layers and nano-rod growth layer.For fabricated an advanced extracellular iron biosensor, the ZnO-(NRs) deposited on plastic and silicon substrates then coated with a thin layer of specificionophore membrane to be used for iron concentration measurements in extracellular solution.The prepared sample crystallinity and microstructure was characterized by x-ray diffraction (XRD) which, implied that ZnO-(NRs)TF sample crystallite sizes are in the nano-scale. The prepared samples morphology was characterized by Field emission scanning electron microscope (FESEM).

Keywords: ZnO-(NRs)TF, Sol gel, aqueous chemical growth, XRD, FESEM and biosensor.

Introduction

Increasing interest in smart technologies directs our attention toward oxide materials such as ZnO as a possible low cost solution for energy needs. ZnO is gaining significant interest due to the ability to be prepared in a highly oriented manner at a low temperature, on different flexible substrates, with associated nano-structured growth and texture [1-3].

Zinc oxide (ZnO) nano-materials such as nano-tube, nano-rods (NRs) and nano-wires have been receiving great attention, where it shows various shapes of ZnOnano-structures that can easily be synthesized by different methods and it have many valuable properties. It can be used for chemical and biological species detection. ZnO-(NRs) based biosensor is one of the important potential applications. (Fe^{3+}) biosensor based on ZnO-(NRs) with selective iron iono-phore (18 crown 6) was reported and studied well previously by our team work and others [1]. ZnO has generated great interest in biosensors due to its many important properties such as being bio-safe, possesses polar surface, their small size and many other properties that facilitate chemical and bio-sensing. Moreover, ZnO is non-toxic has electrochemical activity, chemical stability, and has high electron communication properties [4&5].

The overall aim of this work isto fabricate an advanced extracellular iron biosensor used for iron concentration measurements in extracellular solution

Materials and Methodology

ZnO-(NRs)TF were prepared in two stage (seedsolution and nano-rod growth) by using sol-gel (SG) and aqueous chemical growth (ACG) methods, respectively[6&7].

Seed solution prepared by Sol-Gel method

To obtain the desired morphology and good quality of the material, the substrate was cleaned prior to nano-crystal ZnO thin film deposition as reported previously by our team work [8]. The seed solution was used for the surface modification of substrate which, provides nucleation sights for the growth of nano-structures and helps to enhance the density as well as homogeneity of nano-particles[9]. A coating seed solution was prepared by dissolving zinc acetate dehydrate ($Zn\ (CH_3COO)_2{\cdot}2H_2O$) in mixed Solution of mono-ethanolamine MEA ($NH_2CH_2CH_2OH$) and

*Corresponding author : norallah111@yahoo.com
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2-methoxyethanol at room temperature, however the molar ratio of MEA to zinc acetate was 1:1. The seed solution was stirred at 50°C for 2 h until yielding a clear and homogeneous solution. The mixed solutions were aged at room temperature for another 24 h. Then, the solution was coated on plastic substrate by spin coating with a speed of 3000 rpm for 30 sec. The coating process was repeated several time and dried in open air at room temperature and finally placed in pre-heated laboratory oven at 150^o and 250^{o}C for conducting plastic and silicon substrate, respectively in order to decompose the zinc acetate dehydrate into ZnOnano-particles. In addition the seed solution provides a good control on the alignment and density of the nucleation points that affect the diameter of the synthesized nano-structures.

Growth method

After uniformly coating substrates with ZnO prepared by seed layers, ZnO-(NRs)TF were grown on it using aqueous chemical growth (ACG) method at low temperature. The growth of ZnOnano-rods was achieved by immersing ZnO seed-layer in 150 mL of aqueous solution composed of 0.025 M zinc nitrate ($Zn(NO_3)_2$) and 0.025 M hexamethylenetetramine (HMT, $C_6H_{12}N_4$) in a conventional flask. The reaction temperature was kept at 95^{0}C for 6 h. The position of the substrate inside the solution does affect much on the growth process; however, substratesare being placed in the solution with face toward the bottom of the beaker. Finally, the substrates were removed from the solution, then immediately rinsed with de-ionized water to remove any residual salt from the surface and dried in air at room temperature. The resulting ZnO-(NRs)TF structure was characterized by x-ray diffraction (XRD) and Field emission scanning electron microscope (FESEM), respectively.

Cover ZnO-(NRs) with Ionophor Membrane

For extracellular iron ions measurements, the ZnO-(NRs) on plastic and silicon substrates were coated with a thin layer of ionophore membrane by manual procedure. The ionophore membrane was prepared by the following composition, 18-crown-6(18CE6) [Fluka], it was used for iron ion selectivity; While Dioctylphenylphosphonate (DOPP)[Aldrich] was used as plasticizer. Polyvinylchloride (PVC) [Fluka] was used as the membrane matrix and tetrahydrofuran (THF) [Flika] was used as solvents.

After preparing the ionophore solution, the ZnO-coated dipped two times in it for 5 minutes until a thin film of the membrane was attached to the surface of the ZnO coated the substrates and then drying it for 1 – 2 hours at room temperature. Generally all the sensors were kept at 4˚C when not in use. Theproposed Fe^{3+} sensors were used as working electrodes for the potentiometric measurements in an aqueous solution of $FeCl_3$with a concentration ranging from 10^{-6} M up to 10^{-2} M. An Ag/AgCl was acting as a reference electrode. The output voltage of this experiment for each concentration of $FeCl_3$ solution was recorded by using pHmeter (model 3510)

Results and Discussion

The crystal structure of ZnO-)NRs(TF synthesized by depositing it on the plastic substrate by using seed layers and aqueous solutions was studied through XRD as shown in Fig.1. The intensities of the peaks were measured in2θ° range between 30° and 70°. The result showed that the ZnO)NRs(TF presented a strong diffraction peak at the (002) plane, seen at 2θ° = 34.45°, indicated that it is in pure wurtzite hexagonal phase with high *c*-axis orientations.

Fig. 2(a&b) shows panoramic view images of the ZnO(NRs)TF grown on (a) plastic and (b) silicon substrates with ZnOnano-particles seed layer to provide the possible nucleation for the ZnO-(NRs)TF growth, covering the whole thin film area with uniform density, equal length, vertically aligned along the c-axis (perpendicular to the substrate) and smoothness top surface. ZnO (NRs)TF have a rod-like shape with primarily aligned along the c-axis (perpendicular to the substrate) and hexagonal cross section which is compatible with the obtained XRD results. It is distributed uniformly with an average diameter equal to (63.5 and 42 nm)by deposited it on both plastic and silicon substrates, respectively.We can conclude that the ZnO (NRs)TFdeposited on silicon substrate with seed layers prepared at 250^{o}C are denser and highly oriented more than the deposited one on plastic substrate with seed layers annealed at 150^{o}C.

The obtained FESEM results indicated that the seed layer annealing temperature is directly influenced theZnO (NRs)TFformation. Adjusting the nano-particles Zinc Oxide density film is a very important way to control the nano-rods diameter.

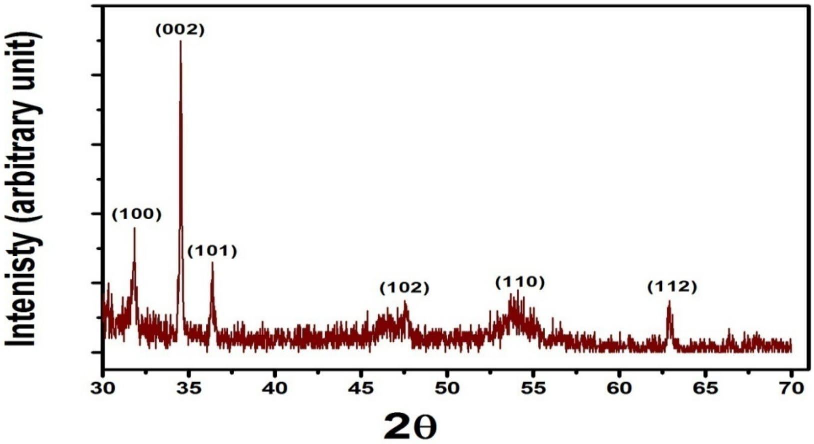
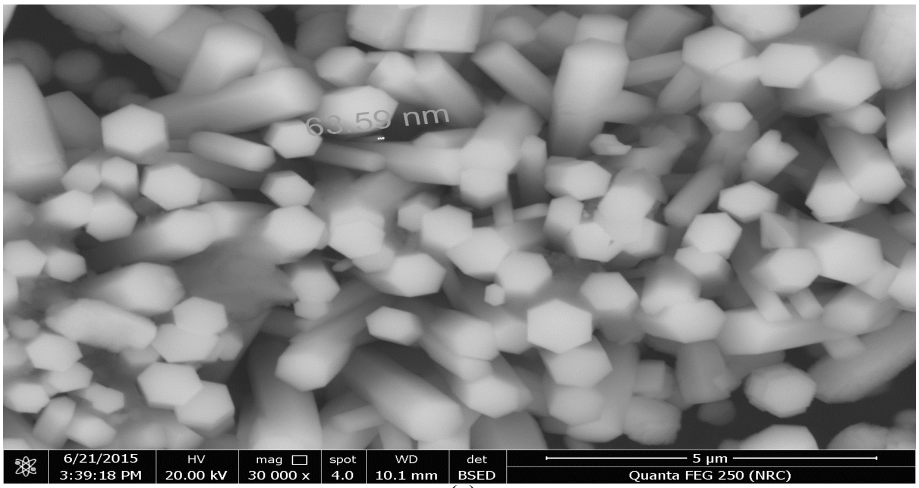
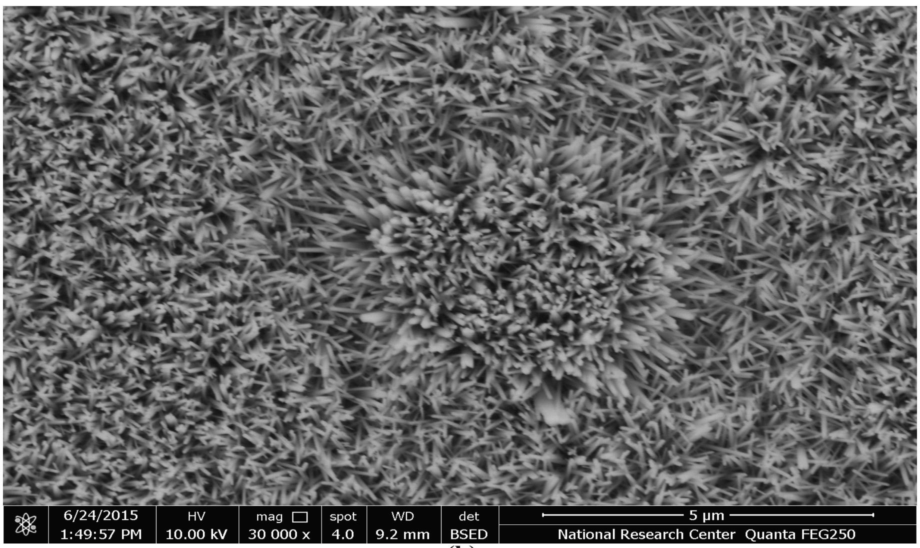


Fig. 1.x-Ray Diffraction of ZnO-(NRs)TF deposited on plastic substrate.



(a)



(b)

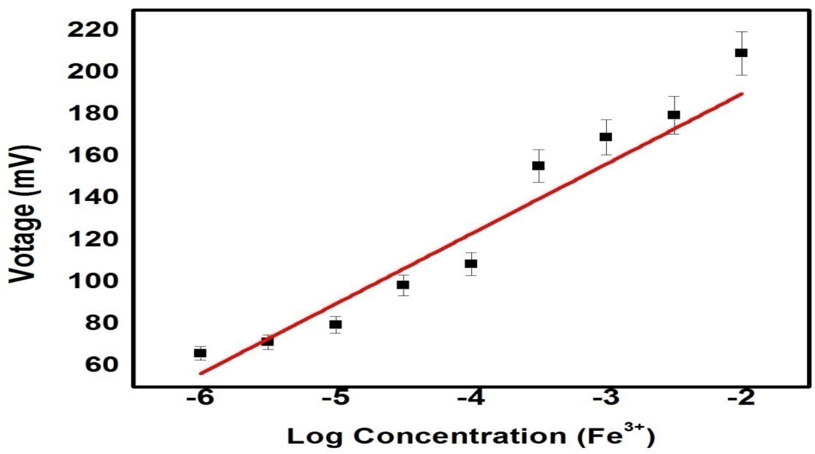
Fig.2 (a&b). FESEM images of ZnO-(NRs)TF grown on (a) plastic substrateannealed at 150^{o}C (b) siliconsubstrates annealed at 250^{o}C, for biosensor application.

In fact the Zinc Oxidenano-rods diameter decreased by increasing the Zinc Oxide nano-particles density, moreoverits orientation becomes better by increasing Zinc Oxide nano-particles density**.** Where the seed solution is used for the nano-rods surface modification and helps to enhance the density as well as particles homogeneity.

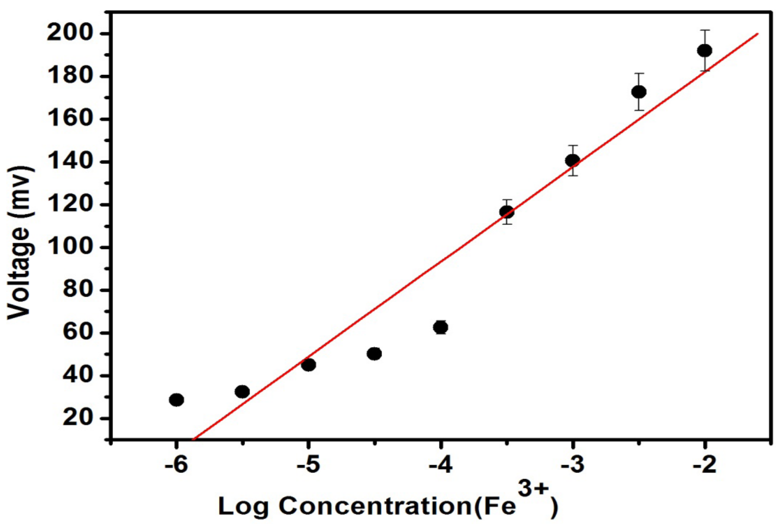
ZnO-(NRs)TF deposited on the mentioned substrates, covered with iron selective membrane can be used asFe^{3+}biosensor to study the iron ions selectivity in an $FeCl_3$ aqueous solutions. For this purpose $FeCl_3$ solutions with concentration ranging from 10^{-6} M up to 10^{-2} M was used for studying the Fe^{3+} ions potentiometric response.

Fig.3 (a&b) showsthe calibration curves for the Fe^{3+} ions concentration in FeCl3 solution as a function of the output voltage response by using ZnO-(NRs)TF deposited on conducting plastic and silicon substrates covered with iron selective membrane as working electrodebiosensors. It is clearly seen that the Fe^{3+} bio-sensor output response showed stable output voltage for the mentioned concentration range.

The electrochemical cell voltage (electromotive force) changes when the tested solutions composition was changed. These changes can be related to the iron ions concentration in the test solution via a calibration procedure.



(a)



(b)

Fig.3(a&b).The calibration curve of the log concentration for Fe^{3+}ionsin $FeCl_3$ solution as a function of electrochemical potential difference by using ZnO-(NRs)TF deposited on(a)conducting Plastic substrate (b) silicon substrate, for bio-sensor application.

A function of the iron ions concentration is a cell voltage in the testing solution. We tested the twoselective Fe^{3+} biosensors in $FeCl_3$ concentrations ranging from 10^{-6} M up to 10^{-2} M of iron electrolytic solution.

The cell potential construction of the tow Fe^{3+} biosensors using ZnO-(NRs)TF deposited on conducting plastic and silicon substrates are presented in the following schemes:

Plastic|ZnO|membrane||$FeCl_3$ electrolyticsolution|| Cl-|AgCl|Ag (1)

Silicon|ZnO|membrane||$FeCl_3$ electrolyticsolution| |Cl-|AgCl|Ag (2)

The iron ion biosensorshavelinearity for a wide concentration range between 10^{-6} M and 10^{-2} M in both biosensors used. The results indicated that the electrode is very sensitive to iron ions giving a slope around 38.16 and 44.39mV/decade with a regression coefficient R^2 = 0.96 and 0.93 for plastic and silicon working electrodes iron biosensors, respectively.

Conclusion

The two methods, Sol-Gel and aqueous chemical growth were successfully used in ZnO (NRs) thin films synthesis with Wurtzite hexagonal structure as revealed from XRD analysis. The ZnO (NRs)TF grown on conducting plasticand siliconsubstrates were found to be distributed uniformly and vertically aligned with diameter 63.5 nm for the former and 42 nm for the later. The overall aim of using the ZnO-(NRs)TF is to introduce a new advanced biosensors technique accurate, easily, faster and sheep by using the nanotechnology to act as iron biosensors for iron ions concentrations measurement.

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القضبان النانو مترية من أكاسيد المواد واستخدامها لتطبيقات الاستشعار الحيوية.

حنان عبد الظاهر عبدالوهاب [1], إيناس كمال بطيشه[1], عزيزة عبدالمنعم السعيد [2], عايدة عبدالكريم سلامه [2]
[1]شعبة الفيزياءالحيوية - قسم الفيزياء- كليةالعلوم- جامعة الازهر(بنات)[2]شعبة البحوث الفيزيقية - قسم فيزيقا الجوامد- المركزالقومي للبحوث-مصر.

الاهتمام المتزايدبالتكنولوجياالذكية يوجهانتباهنانحوأكاسيد الموادمثل مادة أكسيد الزنك (ZnO)), تحظي مادة أكسيد الزنكاهتمامًاكبيرًا نظرًالقدرتهاعلىالتحضيربطرق مختلفه تحت بدرجةحرارةمنخفضة، كما انها يمكن تحضيرها علىركائزمرنةمختلفةبعدة أشكال نانومتريهمختلفة.
خلال هذه الدراسة, يتم تحضير أجهزةاستشعارحيويةلأيونات الحديد اعتمادا علي القضبان النانو مترية من مادة أكسيد الزنك . يتم اختبار اجهزة استشعار الحديد المحضرة في محاليل ذات تركيزات مختلفة من مادة كلوريد الحديد بتركيزات تتراوح من ١٠ -٦ مول الي ١٠ -٢ مول وذالك بطلاء طبقه رقيقة من قضبان اكسيد الزنك النانو مترية علي ركائز البلاستيك الموصلة وعلي ركائز السيليكون لتعمل بمثابة قطب فعال في جهاز استشعار الحديد مقابل قطب كلوريد الفضة المرجعي.
- يتم تحضير قضبان اكسيد الزنك النانومترية باستخدام طريقتي السائل الجيلاتيني و النمو الكميائي المائي, تستخدم طريقة السائل الجيلاتيني لتحضير طبقة البذور التي تبني عليها القضبان النانومترية التي يتم انمائها بطريقة النمو الكميائي المائي.
- دراسة خواص التركيب البللوري والشكل الهيكلي النانومتري لطبقات قضبان الزنك النانومترية المحضرة علي الركائز باستخدام جهاز حيود الاشعه السينية وجهار الميكروسكوب الالكتروني الماسح عالي الدقة, وقد اظهرت النتائج ان المادة هي قضبان اكسيد الزنك ذات الشكل السداسي بقطر ٦٣,٥ نانومتر , بعد ذالك يتم طلاء قضبان اكسيد الزنك النانومترية النامية علي الركائز بطبقه رقيقه من غشاء انتقائي لمادة الحديد ليصبح بذالك القطب جاهز لاستخدامه كقطب فعال في جهاز استشعار الحديد الحيوي.
- باختبار اجهزة استشعار الحديد المحضرة لقياس تركيز ايونات الحديد في محاليل كلوريد الفضة ذات تركيزات مختلفة اظهرت النتائج علاقه خطيه وأشارتالنتائجإلىأنالقطبحساسجدالأيوناتالحديدبمعامل انحدار ٠,٩٦ لركيزة البلاستيك , ٠,٩٣ لركيزة السيليكون .
- يتمثل الهدفالعاممن هذه الدراسة, في استخدام قضبان اكسيد الزنك النانومترية في تقديمتقنيةأجهزةاستشعارمتطورةجديدةدقيقةوسريعةباستخدامتقنيةالنانوللعملكمستشعراتحيويةللحديدلقياستركيزأيوناتالحديد.