Tikrit Journal of Pure Science 21 (6) 2016 *ISSN: 1813 – 1662 (Print)*
E-ISSN: 2415 – 1726 (On Line)

Analytical Study of Zinc Sulphide Electrode Prepared from Nano material

Ali I . Khaleel[1] , Khalaf F. Al-Samarrai[2] , Marwan A. mahmood[1]
[1]*Department of Chemistry , College of Science , University of Tikrit , Tikrit , Iraq*
[2]*Department of Chemistry , College of Education , University of Samarra , Samaraa , Iraq*

Abstract
Zinc Sulphide nanoparticles (NPs) has been prepared from raw material by microwave method. ZnS NPs were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), The size of ZnS NPs were about (3.15nm) calculated from the Scherer formula from the most intense XRD peak, The calculated product for ZnS was about 94.4%.Zn^{2+}-selective electrode based on poly vinyl chloride (PVC) was prepared by using ZnS Nanoparticles (NPs) powders and di-butyl phthalate, and were compared The analytical specifications of ZnS NPs and ZnS Microparticles (Non- NPs) electrode. ZnS NPs electrode and ZnS Non- NPs electrode give linear range upon (10^{-5}-10^{-2})M and (10^{-4}-10^{-2})M, Nernstain slope of (30.35 mV/decade) and (30.84 mV/decade), correlation coefficient of (0.9999) and (0.9995), detection limit of ($1.733x10^{-7}$)M and ($2.486x10^{-6}$)M, quantitative limit of ($5.77x10^{-7}$)M and ($7.07x10^{-6}$)M, the response time of (9-39) second and (13-36) second, respectively. The lifetime for each electrode was 15 days. The optimum conditions for each electrode were (5-7), (20-30℃) and (10^{-4}) M for pH, temperature and concentration of filling solution respectively. The selectivity of electrodes were measured using mixed solutions method, the results showed that the selectivity coefficient values for all interferences ions are less than one.

Key words: Zinc Sulphide, nano material , analytical study, ZnS NPs electrode.

1. Introduction
In the last years, synthesis of materials at nanometric scale has become an important due to the strong dependency of the size of the material particles over their properties: optical, mechanical and electrical[1].The term nanotechnology was defined, the matters have at least one dimension sized from (1-100) nm [2]. Sulphides nonmaterial's (NMs) have a special physical and chemical properties are not available when they are in the normal size [3]. There are serval methods for the preparation of ZnS nanoparticles such as hydrothermal method, sonochemical method, microwave irradiation, and solvothermal method[4-7]. They are used in solar cells, light-emitting diodes, optoelectronic devices, photocatalysis, environmental sensors, and biological sensors
[8]. ZnS has exhibitted various of nanostructures including nanobelts, nanoneedles, nanoflowers, nanorods, nanonails, nanoparticles, nanowires and nanobows [10]. An ion-selective electrodes (ISEs) are defined as an electroanalytical sensor with a membrane whose potential indicates the activity of the ion to be determined in a solution. ISEs have certain undoubted advantages: they do not affect the test solution, they are portable, suitable for direct determinations and as sensors for titrations, and they are not expensive [11]. In this paper, aimed to the preparation of ZnS NPs using microwave method because it is fast, simple, energy-efficient and less time-consuming [12]. And ion selective electrodes of ZnS NPs and ZnS non- NPs were prepared and compared between the analytical specification of these electrodes.

2. Experimental
2.1. Apparatus
Microwave oven (Russell Hobbs-RHM 1714B-England). X-ray Diffraction (XRD) (Shimadzu-6000 Japan). Scanning Electron Microscopy (SEM) (TESCAN-VEGA Easy probe- USA). pH meter (HANNA pH meter-211 Germany). Calomel Electrode. Silver/Silver Chloride Electrode. Electronic Balance (Sartorius Germany). Rdry8i-Ultrasonic bath (DAIHAN Labtech- LUC 405 Korea). Dry oven (Termaks-TS8056 Norway). Muffle (Carbolite-CWF 12/5 England).

2.2. Chemicals
All chemicals used were of high purity and were obtained from BDH, Fluka, GCC, Merck and Riedel-dehaen.

2.3. Stock and Working Solutions
For preparation of solutions, deionized water (DiW) was used. (0.05, 0.1, 0.2, 0.3, 0.4)M of Zinc acetate dehydrate, (0.06)M of thioacetamide, 0.1M of Hydrochloric acid, 0.01M of Potassium chloride, 0.01M of Sodium chloride, 0.01M of Nickel nitrate hexahydrate, 0.01M of Copper chloride, 0.01M of Cadmium sulphate, (10^{-3},10^{-4})M of Zinc chloride dehydrate were prepared by dissolving accurate weight in suitable volume of DW in volumetric flasks.

2.4. Preparation of ZnS NPs
For preparation of ZnS NPs, 50 ml of 0.06 thioacetamide solution and 50 ml of 0.05M Zinc acetate dehydrate solution were mixed slowly, put in microwave, irradiated for 30 min is 560 W, cooled at room temperature and filtered. The obtained white precipitate was washed with ethanol and DW (2-3) times, dried at 110 ℃ for 12 h, after complete drying, powder was crushed using mortar pestle. A precipitate of ZnS NPs was characterized using SEM and XRD Cu Kc (λ = 0.15405nm) incident radiation. XRD patterns were recorded from 30˚to 80˚(2θ).

2.4.1. Optimum Conditions of ZnS NPs Preparation
Inorder to get optimum conditions to prepar of ZnS NPs, several variables were investigated

(concentration of raw material (Zn^{2+} ions), force of radiation and time of radiation).

2.5. Preparation of Electrodes

For preparation of ZnS NPs and ZnS Non- NPs electrodes, a 0.4 gm of PVC dissolved in a mixture composed of 8 ml acetone and 8 ml tetrahydrofuran (THF), then 0.1 gm of ZnS NPs or ZnS Non- NPs were mixed thoroughly for 5 min, and 0.45 ml of di-butyl phthalate as plasticizer material was added and mixed, (dissolution and mixing obtained via ultrasonic bath). The mixture was transferred to the glass petri dish (60 mm diameter) and kept at room temperature for about 24h. The solvent was evaporated slowly until a membrane of about 0.3 mm thick was formed. A desired piece of the membrane was cut and then glued to one end of a Perspex tube (15 mm internal diameter and 9 cm long) using THF solvent. Then, the Perspex tube was filled with an internal filling solution 0.01M of Zinc acetate dehydrates (Zn^{2+} ions). The electrode was finally conditioned for 24h by soaking in a 0.01M of Zn^{2+} ions. A silver/silver chloride electrode was used as the internal reference electrode.

2.6. Construction of Calibration Curve of ZnS Electrodes

Twenty ml of different concentration of Zn^{2+} ions solutions in the range (10^{-6}-10^{-1}) M were placed in series often of 40 ml beakers. Then, the potentials were measured by using the prepared membrane electrodes of ZnS NPs and ZnS Non- NPs at concentration of filling solution of 10^{-4}M, pH (5-7) and T (20 ˚-30℃) for each of ZnS NPs membrane electrode and ZnS Non- NPs membrane electrode.

3. Results and Discussion

3.1. Optimum Conditions of ZnS NPs Preparation

Results Showed that the optimum conditions to prepare of ZnS NPs were (0.05M) Zn^{2+} ions, (30 min) time for radiation (at 560 W), as in figure 1.

3.2. XRD and SEM of ZnS NPs Prepared at the Optimum Conditions

Fig.1 shows XRD pattern of ZnS NPs prepared at the optimum conditions. The mean particles size (D) in nm is calculated by using Scherrer formula [13]:

$$\mathbf{D} = \frac{\mathbf{0.9\,\lambda}}{\boldsymbol{\beta}\,\mathbf{COS\theta}} \qquad \text{Eq. (1)}$$

Where $\boldsymbol{\lambda}$ is the X-ray wavelength (λ = 0.15405nm), β is the full width at half maximum (FWHM – in radian) at a selected 2θ. The XRD results of ZnS NPs were: the peaks at 2θ = 26.5207, 43.8680, 51.9873 at FWHM = (0.5619, 0.7133 ˚and 0.7200˚) at a selected 2θ respectively. The mean particles size of ZnS NPs was about 3.15 nm. Fig.2 shows SEM of ZnS NPs prepared at the optimum conditions.

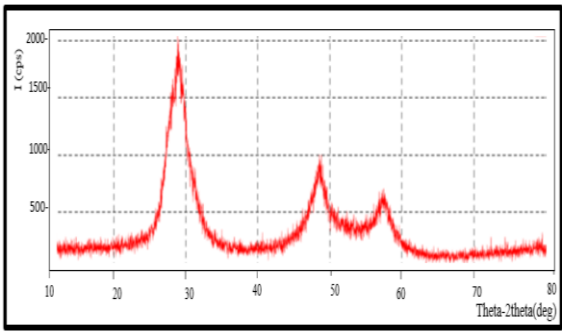


Fig. 1: XRD pattern of ZnS NPs

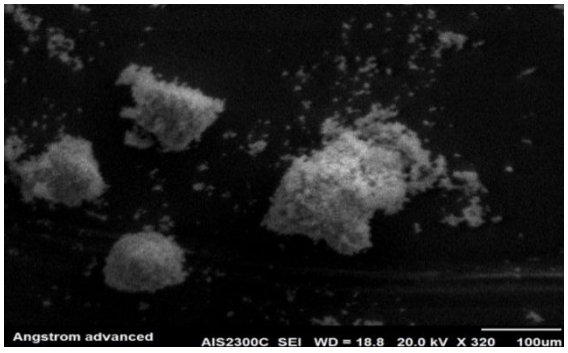
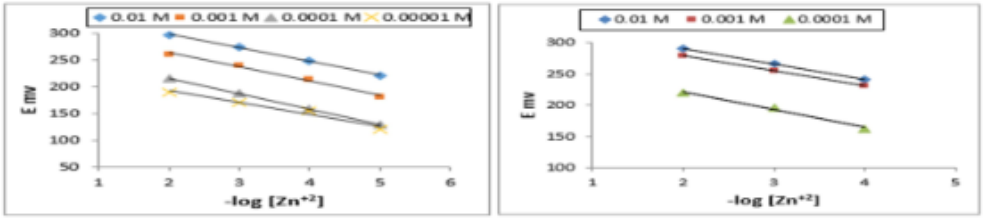


Fig. 2: SEM of ZnS NPs

3.3. Optimum Conditions of ZnS NPs and Non-NPs Electrodes Working

Figures 3-5 and table 1 show the effect concentration of filling solution, pH, temperature and time on the response of electrodes. The optimum concentration of filling solution was 10^{-4} M for two electrodes. pH range (5-7) for to electrodes and the observed potential drift at low pH (<5) may be attributed to the membrane response to H^{+} ions and at higher pH values (>7. The effect of temperature was small and not affect the electrodes responses so the temperature range (20-30)℃ was adapted. The response times were (9-39) second at concentration (10^{-5}-10^{-2})M and (13-36) second at concentration (10^{-4}-10^{-2})M for ZnS NPs and ZnS Non- NPs respectively.



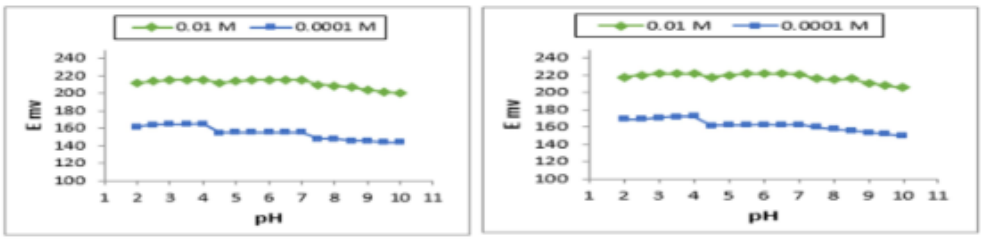
3(a) 3(b)

Fig. 3: effect of filling solution Concentration on: (a) ZnS NPs electrode response and (b) ZnS Non- NPs electrode response

ISSN: 1813 – 1662 (Print)
E-ISSN: 2415 – 1726 (On Line)

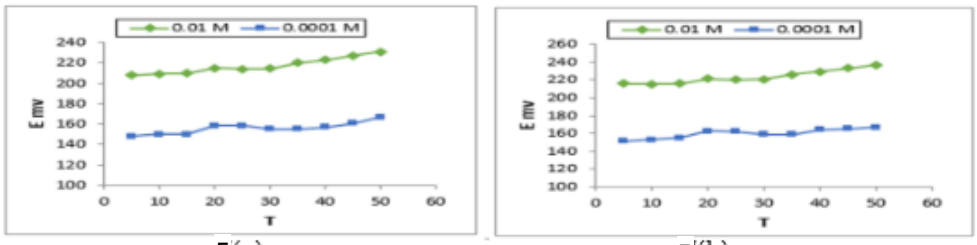
Table 1: Concentration effect of filling solution of electrodes response for ZnS NPs and Non- NPs

parameters	ZnS NPs electrode				ZnS Non- NPs electrode		
Filling solution (M)	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-2}	10^{-3}	10^{-4}
Slope (mV/decade)	25.1	26.6	28.86	22.51	24.5	24.35	28.65



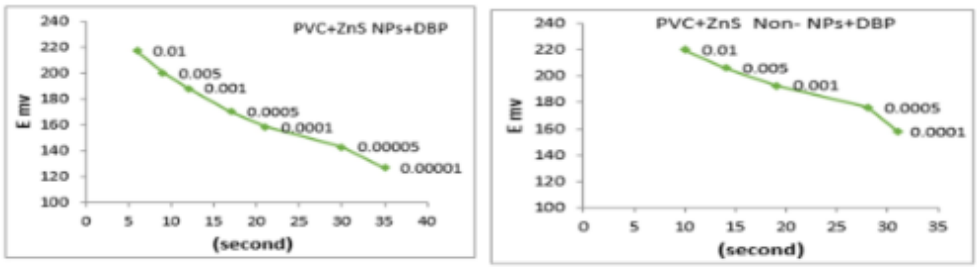
4 (a) 4 (b)

Fig. 4: pH effect on electrode response of: (a) ZnS NPs and (b) ZnS Non- NPs



5(a) 5'(b)

Fig. 5: Temperature effect on electrode response of: (a) ZnS NPs and (b) ZnS Non- NPs

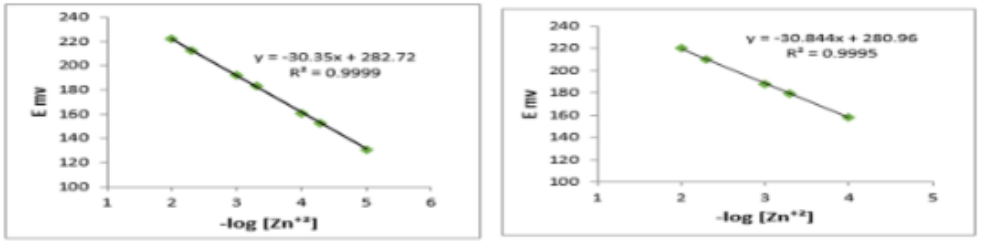


6 (a) 6 (b)

Fig. 6: Response time of: (a) ZnS NPs electrode and (b) ZnS Non- NPs electrode

3.5. Calibration Curve of ZnS Electrodes

Figures 7(a) and 7(b) showed the linearity of ZnS NPs electrode (10^{-5}-10^{-2})M was best than of ZnS Non- NPs electrode (10^{-4}-10^{-2})M and the nernstian slopes were 30.35 mV/decade and 30.84 mV/decade for ZnS NPs electrode and ZnS Non- NPs electrode respectively. That's to say the nernstian slope of ZnS NPs electrode is nearest to real value (29.58 mV/decade).



7(a) 7(b)

Fig. 7: Calibration curve of: (a) ZnS NPs electrode for [Zn^{2+}] (10^{-5}-10^{-2}) M and (b) ZnS Non- NPs electrode for [Zn^{2+}] (10^{-4}-10^{-2})M

Table 2 shows the accuracy and precision of the calibration curves.

Table 2: The accuracy and precision of the calibration curves

Type electrode	Conc. of Zn^{2+} (M)	Potential[a] (mV)	Conc. found (M)	RSD %	RE %	Rec %
ZnS NPs electrode	10^{-2}	222	$0.998x10^{-2}$	0.625	- 0.16	99.84
	10^{-3}	192	$1.025x10^{-3}$	0.314	2.53	102.53
ZnS Non- NPs electrode	10^{-2}	220	$1.055x10^{-2}$	0.556	5.58	105.58
	10^{-3}	188	$0.968x10^{-3}$	0.651	-3.15	96.85

[a] Average of seven determinations.

The results showed the recovery percentages and RSD of 10^{-2} and 10^{-3}M by using ZnS NPs electrode were 99.84%, 0.625 and 102.53%, 0.314 while for ZnS Non- NPs electrode were 105.53%, 0.556 and 105.58%, 0.651 respectively. The detection limit and quantitative limit for ZnS NPs electrode were $1.733x10^{-7}$M and $5.77x10^{-7}$M while for ZnS Non-NPs electrode were $2.486x10^{-6}$M and $7.07x10^{-6}$M respectively, these results give advantage to the ZnS NPs electrode.

3.6. Selectivity of ZnS Electrodes

The selectivity coefficient ($K_{A,B}^{Pot}$) of ZnS NPs and ZnS Non- NPs electrodes for determination of Zn^{2+} ions in presence of different cations and anions were determined by using mixed solution method. The concentrations of Zn^{2+} ions were (10^{-2},10^{-3})M and the concentrations of interfering ions were 10^{-2}M. The calculation formula of ($K_{A,B}^{Pot}$) is as follows when the concentration of Zn^{2+} ion and interfering ion are equal [14]:

$$K_{A,B}^{Pot} = \frac{C_{A\ min} \times P}{C_{B\ max} \times 100} \qquad \text{Eq. (2)}$$

Where , $K_{A,B}^{Pot}$ is selectivity coefficient of sample ion (A) towards interfering ion (B) , $C_{A\ min}$ is alower concentration of sample ion, $C_{B\ max}$ is a higher concentration of interfering ion, P is the relative error of ion sample (A) towards interfering ion (B). Table 3 shows the values of selectivity coefficient ($K_{A,B}^{Pot}$) of ZnS electrodes for determination of Zn^{2+} ions.

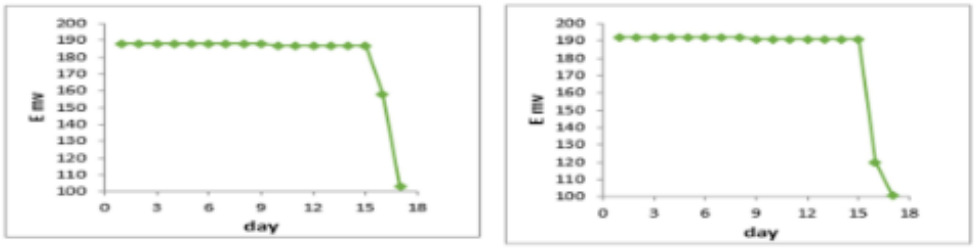
Table 3: Values of selectivity coefficient of ZnS electrodes for determination Zn^{2+} ions

Interfering ion of 10^{-2} M	Values of $K_{A,B}^{Pot}$			
	ZnS NPs electrode		ZnS Non- NPs electrode	
	Conc. of Zn^{2+} (M)		Conc. of Zn^{2+} (M)	
	10^{-2}	10^{-3}	10^{-2}	10^{-3}
K^{+1}	0.0067	0.0002	0.009	0.0005
Na^{+1}	0.0022	0.0010	0.0068	0.0012
Ni^{+2}	-0.0067	0.0020−	0.018	−0.0010
Cd^{+2}	-0.009	-0.0013	0.015	0.0021
Cu^{+2}	-0.0135	-0.0010	0.090	-0.0029

According to values of selectivity coefficient which was less than one, the interfering of cations and anions could not affect on the selectivity of ZnS electrodes, and the ZnS NPs electrode give better selectivity than ZnS Non- NPs electrode as in table3.

3.7. Lifetime of ZnS Electrodes

Figures 8(a) and 8(b) show the lifetime of ZnS NPs and ZnS Non- NPs electrodes. The lifetime for each of ZnS NPs electrode and ZnS Non- NPs electrode were 15 days.



8 (a) 8 (b)

Fig. 8: Lifetime of : (a) ZnS NPs electrode and (b) ZnS Non- NPs electrode

3.8. Analytical Applications of ZnS Electrodes

The concentrations (10^{-3}, 10^{-4}) M of the unknown (Zn^{2+} ions in Zinc chloride dehydrate solution) by using direct method was calculated throw linear equation of the calibration curve for each of ZnS NPs electrode and ZnS Non- NPs electrode, as in table 4, and The concentration 10^{-4}M of the unknown (Zn^{2+} ions in Zinc chloride dehydrate solution) by using

multiple standard addition method was calculated by the following equation [15]:

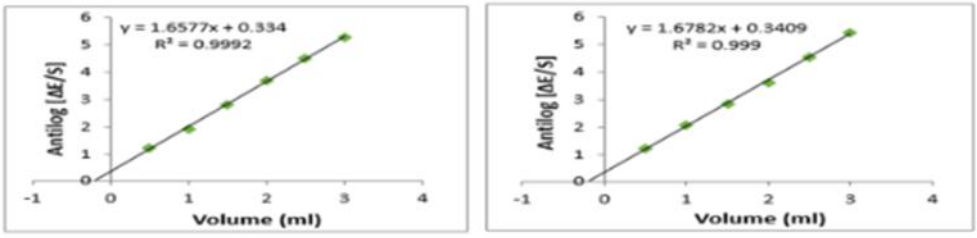
$C_x V_x = -V_e C_s$ Eq. (3)

Where, C_x is the concentration of unknown, C_s is the added concentration of Zinc acetate dehydrate (10^{-2} M), V_x is the volume of unknown (20 ml), V_e is the value (ml) at intercept with X axis (V_e calculated from linear equation of calibration curve of multiple standard addition method when y = 0). As in table 5 and figures 9(a) and 9(b).

Table 4: Application results using direct method for determination Zn^{2+} ions in Zinc chloride dehydrate

Type electrode	Conc. of Zn^{2+} (M)	Potential[a] (mV)	Conc. Found (M)	RSD %	RE %	Rec. %
ZnS NPs electrode	10^{-3}	191.61	$0.9957x10^{-3}$	0.4207	– 0.43	99.57
	10^{-4}	161.4	$1.0060x10^{-4}$	0.4683	0.60	100.60
ZnS Non- NPs electrode	10^{-3}	188.2	$0.9831x10^{-3}$	0.6376	– 1.69	98.31
	10^{-4}	157.4	$0.9863x10^{-4}$	0.7714	– 1.37	98.63

[a] Average of seven determination



9 (a) 9 (b)

Fig. 9: Calibration curve by multiple standard addition method for determination Zn^{2+} ions in Zinc chloride dihydrate (10^{-4}M) by using: (a) ZnS NPs electrode and (b) ZnS Non- NPs electrode

Table 5: Application results using multiple standard addition method for determination Zn^{2+} ions in Zinc chloride dihydrate (10^{-4}M)

Type electrode	Conc. of Zn^{2+} (M)	Conc. found (M)	RSD %	RE %	Rec %
ZnS NPs electrode	10^{-4}	$1.007x10^{-4}$	0.432	+ 0.7	100.7
ZnS Non- NPs electrode	10^{-4}	$1.015x10^{-4}$	0.6232	+ 1.5	101.5

In two methods the accuracy and precision of ZnS NPs electrode were best than ZnS Non- NPs electrode, these results may be due to the properties of NPs are not in Non- NPs .

4. Conclusion

ZnS NPs have been successfully prepared by using microwave method. The average particles size of ZnS NPs was about 3.15 nm. ZnS NPs electrode and ZnS Non- NPs electrode have been successfully prepared. The calibration curve and analytical results of ZnS NPs electrode were best comparison with calibration curve and analytical results of ZnS Non- NPs electrode. Electrodes were applied successfully to determination Zn (II) ions in its solutions, with preference to the ZnS NPs electrode in all of the surveyed.

References

[1] S. Murugesan, T. Park, H. Yang, S. Mousa and R. J. Linhardt, Langmuir 22(8) (2006) 3461-3463.
[2] D. Shailaja, M. Shailaja, P. Roselin, J. Manasa and N. Shalini, Int. J. Bioassays 2(6)(2013)914-917.
[3] B. Gilbert, F. Huang, H. Zhang, GA. Waychunas and JF. Banfield, Science, 305(5684)(2004) 651-654.
[4] L. Zhang, D. Qin, G. Yang, and Q. Zhang, Chalcogenide Letter 9 (93) (2012).
[5] L. Chai, J. Phys, Y. Zhu, H.Li,S. Xiong,Y, Qian. Chem. C. 111 (12658) (2007).
[6] J. Q. Sun, X. P. Shen, K. M. Chen, Q. Liu, and W. Liu. Solid State Commun. 147(501) (2008).
[7] L. Wang, L. Chen, T. Luo, and Y. Qian, Mater Lett. 60 (3627) (2006).
[8] N. Ghows M.H. Entezari, Ultrason Sonochem. 18 (269) (2010).
[9] M. Kooti and A.N. Sedeh, J. of Chemistry 2013 (2013) 1-4
[10] A. Eftekhari, F. Molaei and H. Arami, Materials Science and Engineering A 437 (2) (2006) 446-450
[11] J. Koryta, J. Annu. Rev. Mater. Sci. 16 (1986) 13-27
[12] A. Roy and J. Bhattacharya, International Journal of Nanoscience 10 (3) (2011) 413-418
[13] M. Lashanizadegan and H. Mirzazadeh, Journal of Ceramic Processing Research 13 (4) (2012) 389-391
[14] P.L. Bailey, Analysis with ion selective electrodes, Heyden international topics in science, London, 2nd edition (1980).
[15] P. Grundler, Chemical sensors, an introduction for scientists and engineers, Springer- Verlag, Berlin, Heidelberg (2007) .

Tikrit Journal of Pure Science 21 (6) 2016 *ISSN: 1813 – 1662 (Print)*
E-ISSN: 2415 – 1726 (On Line)

دراسة تحليلية لتحضير قطب كبريتيد الزنك من مادة نانوية

علي أبراهيم خليل[1] ، خلف فارس عطية[2] ، مروان عدنان محمود[1]

[1]قسم الكيمياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

[2]قسم الكيمياء ، كلية التربية ، جامعة سامراء ، سامراء ، العراق

الملخص

كبريتيد الزنك النانوي تم تحضيره من مواده الأولية بواسطة المايكروويف وتم تشخيص هذا الكبريتيد النانوي بوساطة حيود الأشعة السينية (XRD)، والمجهر الالكتروني الماسح (SEM) وان حجم الدقائق المحضرة لكبريتيد الزنك النانوي كانت 3.15 nm وذلك باستعمال صيغة ديباي شيرر (Debye Scherrer formula) وبأخذ أعلى شدة في طيف XRD. وحساب كمية المنتوج للكبريتيد المحضر حيث كانت النسبة المؤية لكبريتيد الزنك النانوي (94.4)%. وتم تصنيع أقطاب غشائية انتقائية أيونية لكل من كبريتيد الزنك النانوي والغير نانوي للمقارنة التحليلية ما بين القطبين وذلك باستعمال المادة الملدنة داي بيوتايل فثالات (DBP) والبوليمر متعدد كلوريد الفنيل (PVC) كركيزة لهذه الأقطاب، فضلاً عن إجراء مقارنة بين المواصفات التحليلية لقطب كبريتيد الزنك النانوي وقطب كبريتيد الزنك الغير نانوي .قطب غشاء كبريتيد الزنك النانوي وقطب كبريتيد الزنك الغير نانوي كان لهم الاستجابة الخطية بين (10^{-5} −10^{-2}) M و(10^{-4} −10^{-2}) والميل النرنيستي (30.35 mV/decade) و (30.84 mV/decade) ومعامل الارتباط (0.9999) و(0.9995) وحد الكشف ($1.733x10^{-7}$) M و($2.486x10^{-6}$) M والحد الكمي ($5.77x10^{-7}$) M و ($7.07x10^{-6}$) M وزمن الاستجابة (9−39) ثانية و (13−36) ثانية، على التوالي. وكان العمر الزمني لكل قطب (15) يوم. والظروف المثلى لكل قطب كانت (5−7) (20−30) م (10^{-4}) للدالة الحامضية ودرجة الحرارة والتركيز لمحلول الملء الداخلي على التوالي. وكانت الاقطاب انتقائية باستخدام المحاليل الممزوجة حيث أظهرت النتائج ان قيم معامل الانتقائية للمتداخلات الايونية اقل من واحد.