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Analytical Study of Ion –Selective Electrodes Using Nanoparticulate ZnO

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Abstract

Zinc Oxide nanoparticles (NPs) were prepared from raw materials via a microwave-assisted method. The ZnO NPs were characterized by X-ray Diffraction (XRD) and scanning electron microscopy (SEM). NPs were approximately 22.5 nm in size, as calculated using the Scherrer formula from the most intense XRD peak. The ZnO NPs were compared with ZnO microparticles (MPs) through thermal analysis (thermogravimetry TG, derivative thermogravimetry DTG, and differential thermal analysis DTA). A Zn^{2+}-selective electrode based on polyvinyl chloride was prepared using ZnO NP powder and di-butyl phthalate, and then the analytical specifications of the ZnO NP and ZnO MP electrodes were compared. The ZnO NPs and ZnO MPs electrodes respectively had linear ranges of 10^{-2}–10^{-5} and 10^{-2}–10^{-4} M, Nernstain slopes of 28.71 and 27.79 mV/decade, correlation coefficients of 0.999 and 0.999, detection limits of 1.371×10^{-7} and 2.513×10^{-6} M, quantitative limits of 4.569×10^{-7} and 8.383×10^{-6} M, and response times of 9–39 and 13–36 s respectively. The lifetime of each electrode was 11 day. The optimum conditions for each electrode were pH 5–8, 25–30 °C temperature, and 10^{-3} M filling solution concentration. The selectivity of the electrodes was measured in different solutions, and results showed that the selectivity coefficient values for all interference ions were less than one.

Keywords: Nanoparticles; Electrode; Analysis.
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1. Introduction

Metal oxide Nanoparticles (NPs) have special physical and chemical properties that are not available in their bulk counterparts [1]. Metal oxide NPs are used as catalysts and starting materials ceramics [2]. Nanometer-sized ZnO has many applications in photocatalysis, chemical remediation, photoinitiation polymerization reaction, quantum dot devices, solar energy conversion, biochemical sensors, chemical electrodes, cosmetics and

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pigments [3-8]. ZnO NPs are produced via sol-gel, chemical vapor deposition, direct precipitation, hydrothermal/thermal decomposition, emulsion precipitation, and spray pyrolysis [8]. ZnO exhibits various morphologies including nanobelts, nanoneedles, nanoflowers, nanorods, nanonails, nanoparticles, nanowires and nanobows [9].

An ion-selective electrode (ISE) is an electroanalytical sensor with a membrane whose potential indicates the activity of the ion to be determined in a solution. ISEs are useful because they don't affect the test solution; moreover, they are portable, suitable for direct determinations and titrations, and in expensive [10]. In this paper, we report the preparation of ZnO NPs using a fast, simple, and energy efficient microwave-assisted method [11]. ISEs ZnO NPs and ZnO MPs were prepared, and the analytical specifications were compared.

2. Experimental

The equipment used in this study are the following: microwave oven (Russell Hobbs-RHM 1714B, England), X-ray diffractometer (Shimadzu-6000, Japan), scanning electron microscope (TESCAN-VEGA Easy probe, USA), thermal analyzer (Diamond TG/DTA model (SII) Perkin-Elmer), pH meter (HANNA pH meter-211, Germany), calomel electrode, silver/silver chloride electrode, electronic balance (Sartorius Germany), ultrasonic bath (DAIHAN Labtech-LUC 405, Korea), dry oven (Termaks-TS8056, Norway), and muffle furnace (Carbolite-CWF 12/5, England).

All chemicals used were obtained from BDH, Fluka, GCC, Merck and Riedel-dehaen.

2.1 Stock and Working Solutions

Deionized water (DW) was used to prepare various solutions involving zinc acetate (anhydrous), sodium hydroxide, potassium chloride, sodium chloride, nickel nitrate hexa hydrate, magnesium sulfate, cadmium sulfate and Zinc chloride (anhydrous).

2.2 Preparation of ZnO NPs

ZnO NPs were prepared using 100 mL of 0.4M sodium hydroxide solution and 50 mL of 0.2M zinc acetate dehydrate solution slowly mixed, stirred for 40 min at pH 12.9, and then placed in a microwave. The solution was initially irradiated with 420 W for 20 min and then with 560 W for 30 min, followed by cooling to room temperature and then filtration. The white precipitate, so obtained, was washed two to three times with DW, and then dried at 95℃ for 70 min. After complete drying, powder was crushed using a mortar and pestle and then calcinated at 500℃ for 1h. The as prepared precipitate of the ZnO NPs was characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) with Cu Kc (λ = 0.15405nm) incident radiation. The XRD patterns were as recorded from 30˚to 80˚(2θ).

2.3 Optimum Conditions for ZnO NP Preparation

To obtain the optimum conditions for preparing ZnO NPs, several parameters including raw material (Zn^{2+} ions) concentration, microwave power, radiation time and mixing time.

2.4 Preparation of Electrodes

For the preparation of the ZnO NP and ZnO MP electrodes, 0.4 g of PVC was dissolved in a mixture of 8 mL acetone and 8 mL of tetrahydrofuran (THF), and then 0.1 g of ZnO NPs or ZnO MPs was thoroughly mixed for 5 min. Exactly 0.45 ml of di-butyl phthalate as a plasticizer material was added and mixed. The dissolution and mixing were carried out with an ultrasonic bath. The mixture was transferred to a glass Petri dish and then stored at room temperature for 24 h. The solvent was slowly evaporated until a membrane approximately 0.3 mm thickness was formed. This membrane was cut into the desired thickness and then carefully glued to one end of a Perspex tube (15 mm internal diameter and 9 cm long) using THF. The Perspex tube was filled with 0.01M zinc acetate dehydrates (Zn^{2+} ions). The electrode was finally conditioned for 24h by soaking in 0.01M Zn^{2+} ions. A silver/silver chloride electrode was used as an internal reference.

2.5 Construction of Calibration Curve of ZnO Electrodes

Exactly 20 mL of Zn^{2+} ions solutions at different concentrations in the range of 10^{-6}-10^{-1} M was placed in a beaker. The potentials were measured using ZnO NP and ZnO MP membrane electrodes at 10^{-3} M filling solution concentration, pH 5-8, and T 25 ˚-30℃ for each membrane electrode.

3. Results and Discussion

3.1. Optimum Conditions of ZnO NPs Preparation

The optimum conditions for the preparation of ZnO NPs were as follows: 0.2 M Zn^{2+} ions concentration, 40 minutes mixing time, and two step radiation at 420 W for 20 minutes and 560 W for 30 minutes.

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

Figure.1 shows the XRD pattern of the ZnO NPs prepared at the optimum conditions. The mean particle size (D) in nm was calculated using the Scherrer formula [12]:

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

Where $\boldsymbol{\lambda}$ is the X-ray wavelength (λ = 0.15405nm) and β is the full width at half maximum (FWHM in radian) at a selected 2θ.. The mean particles size of the ZnO NPs was approximately 22.5 nm. Figure 2 shows the SEM image of the ZnO NPs prepared at the optimum conditions.

3.3. Thermal Analysis of ZnO NPs and ZnO MPs

The thermal analysis result of ZnO NPs and ZnO MPs by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) are displayed in Figures 3 and 4. Results showed that the surface area of the ZnO NPs was larger than that of the ZnO MPs. The thermal analysis of the NPs began at room temperature until the final heating with slow steps. By contrast, the analysis of the MPs was delayed until 202℃, after

which a sharp weight loss occurred and finished at 301.7˚C. This result indicates that the NPs are more stable than the MPs.

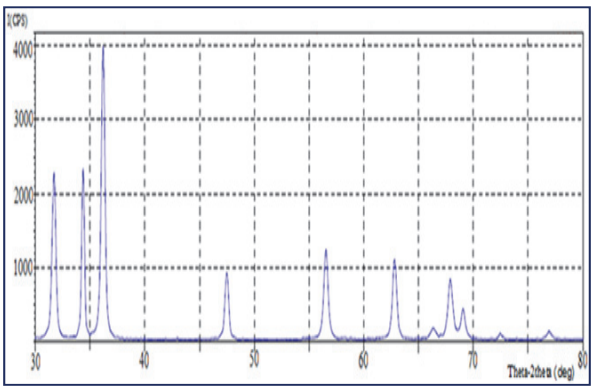


Fig. 1: XRD pattern of ZnO NPs

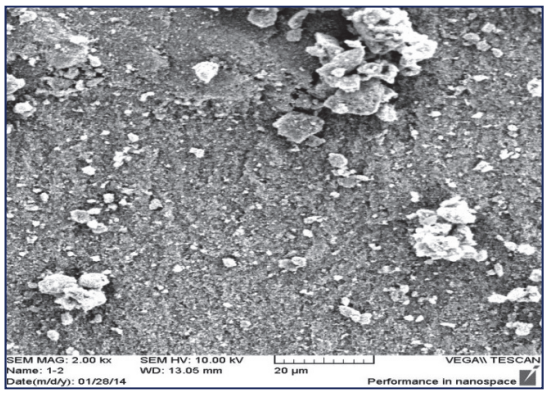


Fig. 2: SEM of ZnO NPs

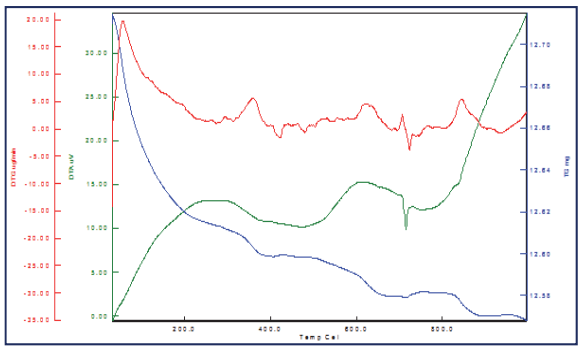


Fig. 3: Thermal analysis curves of ZnO NPs

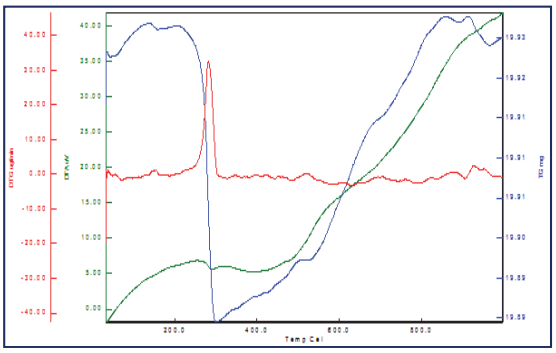


Fig. 4: Thermal analysis curves of ZnO MPs

3.4. Optimum Conditions and life time of ZnO NPs and MPs Electrodes Working

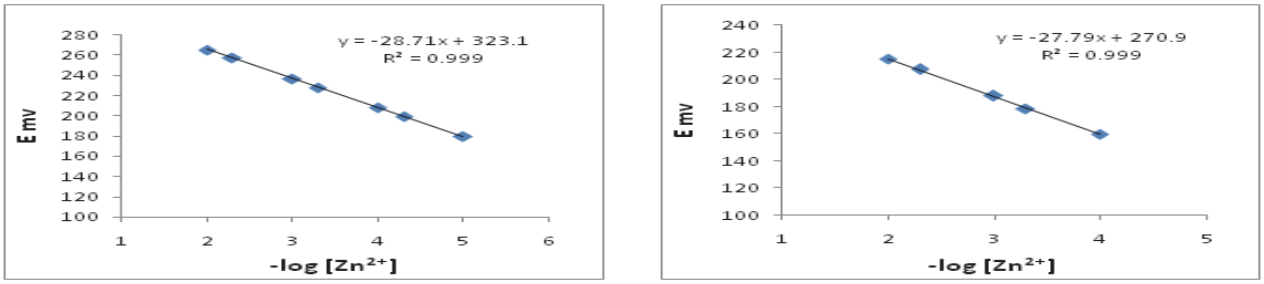
Table 1 shows the effect of filling solution concentration, pH, temperature, and time on electrode response. The optimum filling solution concentration was 10^{-3} M for the two electrodes. At pH 5-8 for the electrodes, the observed potential drift at low pH (<5) may be attributed to the membrane response to H^+ ions, whereas that at high pH (>8) due to the formation of certain hydroxyl complexes of Zn^{2+} ions in the solution [13]. Temperature did not affect the electrodes responses; thus, the temperature range of 25-30℃ was employed. The response times were 9-39 s at 10^{-5}-10^{-2} M concentration and at 13-36 s at 10^{-4}-10^{-2} M concentration for the ZnO NPs and ZnO MPs, respectively.

Table 1: Concentration effect of filling solution of electrodes response and life time for ZnO NPs and MPs

parameters	ZnO NPs electrode				ZnO MPs electrode		
Filling solution (M)	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-2}	10^{-3}	10^{-4}
Slope (mV/decade)	25.1	28.22	26.9	23.2	24	26.25	23.25
Life time(day)	11				11		

3.5. Calibration Curve of ZnO Electrodes

The linearity of the ZnO NP electrode(10^{-5}–10^{-2} M) was better than of the ZnO MP electrode of the ZnO MP electrode (10^{-4}–10^{-2} M) and that the Nernstian slopes were 28.71 and 27.79 mV/decade for the ZnO NP and ZnO MP electrodes, respectively. Thus, the Nernstian slope of the ZnO NP electrode was closer to the real value (29.58 mV/decade) than that of the ZnO MP electrode as in figures 9(a) and 9(b). Table 2 shows the accuracy and precision of the calibration curves.



9a 9b

Fig. 9: Calibration curve of: (a) ZnO NPs electrode for [Zn^{2+}] (10^{-5}-10^{-2}) M and (b) ZnO MPs electrode for [Zn^{2+}] (10^{-4}-10^{-2})M

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%
ZnO NPs electrode	10^{-2}	265.5	$0.986x10^{-2}$	0.424	- 1.4	98.6
	10^{-3}	236.8	$0.987x10^{-3}$	0.356	- 1.3	98.7
ZnO MPs electrode	10^{-2}	215	$0.974x10^{-2}$	0.885	- 2.6	97.4
	10^{-3}	187.9	$1.031x10^{-3}$	0.704	+ 3.1	103.1

[a] Average of seven determinations.

The recovery percentages and RSD for 10^{-2} and 10^{-3} M using the ZnO NP electrode were 98.6%, 0.424 and 98.7%, 0.356, respectively, whereas those for the ZnO MP electrode were 97.4%, 0.885 and 103.1%, 0.704, respectively. The detection and quantitative limits for the ZnO NP electrode were 1.371×10^{-7} and 4.569×10^{-7} M, whereas those for the ZnO MP electrode were 2.513×10^{-6} and 8.383×10^{-6} M, respectively. These results show the advantage of the ZnO NP electrode over the ZnO MP electrode.

3.6. Selectivity of ZnO Electrodes

The selectivity coefficients ($K_{A,B}^{Pot}$) of the ZnO NP and ZnO MP electrodes for the determination of Zn^{2+} ions in the presence of different cations and anions were determined using the mixed solution method. The concentrations of Zn^{2+} ions were 10^{-2} and 10^{-3} M, and those of interfering ions were 10^{-2} M. The calculation formula for ($K_{A,B}^{Pot}$) is as follows when the concentrations of Zn^{2+} and interfering ions 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 the selectivity coefficient of the sample ion (A) toward the interfering ion (B), $C_{A\ min}$ is the low concentration of the sample ion, $C_{B\ max}$ is the high concentration of the interfering ion, and P is the relative error of the sample ion (A) toward the interfering ion (B). Table 3 shows the selectivity coefficients ($K_{A,B}^{Pot}$) of the ZnO electrodes for Zn^{2+} ion determination. On the basis of the selectivity coefficients, which were less than one, the interference of cations and anions could not affect the selectivity of the ZnO electrodes, and the ZnO NP electrode exhibited better selectivity than the ZnO MP electrode (Table 3).

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

Interfering ion of 10^{-2} M	Values of $K_{A,B}^{Pot}$			
	ZnO NPs electrode		ZnO MPs electrode	
	Conc. of Zn^{2+} (M)		Conc. of Zn^{2+} (M)	
	10^{-2}	10^{-3}	10^{-2}	10^{-3}
K^+	- 0.442	- 0.0054	- 0.0612	- 0.0067
Cl^-	- 0.0231	- 0.0034	- 0.0437	- 0.0053
Ni^{2+}	0.0321	0.0049	0.0453	0.006
Cd^{2+}	- 0.0112	- 0.0023	- 0.0339	- 0.0041
SO_4^{2-}	- 0.0124	- 0.0032	- 0.0177	- 0.0036

3.7. Analytical Applications of ZnO Electrodes

The concentrations (10^{-3} and 10^{-4} M) of the unknown (Zn^{2+} ions in zinc chloride dihydrate solution) were calculated using a direct method from the linear equation of the calibration curve of each ZnO NP and ZnO MP electrode (Table 4). The concentration (10^{-4} M) of the unknown (Zn^{2+} ions in zinc chloride dihydrate solution) was calculated through multiple standard additions using the following equation [15]:

$$C_x\ V_x = -\ V_e\ C_s \qquad \text{Eq. (3)}$$

where C_x is the concentration of the unknown, C_s is the added concentration of zinc acetate dihydrate (10^{-2} M), V_x is the volume of the unknown (20 mL), and V_e is the volume (mL) at the X intercept (V_e is calculated from the linear equation of the calibration curve of multiple standard addition when $y = 0$). The results are shown in Table 5 In the two methods, the accuracy and precision of the ZnO NP electrode were better than those of the ZnO MP electrode probably because of the properties of the NPs that are lacking in the MPs.

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.%
ZnO NPs electrode	10^{-3}	237.1	$1.01x10^{-3}$	0.479	+ 1	101
	10^{-4}	208.45	$1.015x10^{-4}$	0.302	+ 1.5	101.5
ZnO MPs electrode	10^{-3}	188	$1.04x10^{-3}$	0.797	+ 4	104
	10^{-4}	160.15	$1.035x10^{-4}$	0.563	+ 3.5	103.5

[a] Average of seven determination

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%
ZnO NPs electrode	10^{-4}	$1.009x10^{-4}$	0.392	+ 0.9	100.9
ZnO MPs electrode	10^{-4}	$1.031x10^{-4}$	0.551	+ 3.1	103.1

4. Conclusion

ZnO NPs were successfully prepared via a microwave-assisted method. The average particle size of the ZnO NPs was approximately 22.5 nm. Thermal analysis demonstrated that the ZnO NPs were more thermally stable than the ZnO MPs. The calibration curve and analytical results of the ZnO NP electrode were better than those of the ZnO MP electrode. The electrodes were successfully applied to determine Zn^{2+} ions in solutions, with preference to the ZnO NP electrode in all samples surveyed.

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