Zinc oxide and Zinc oxide Nanoparticles Carbon Paste Ion Selective Electrode: A Cyclic Voltammetry Comparison Study

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Abstract. Alternative, low-cost, high-Precision, and selectivity methods A new homework ion selective electrodes ISE for zinc metal determination and comparison between size particles in sensitive and selectivity. A hydrothermal method used to prepare zinc oxide nano particles, and use Scanning electromagnetic method TEM for morphology and determined size of ZnO-NPs.

and study the redox of Zn^{2+} in pharma drugs by cyclic voltammetry. (Epa - Epc) > 200 mV, refer to the quasi-reversible mechanism. Physical and chemical properties was study for the electrode in the range of temperature 10-40 °C. voltammograms data showed the negative shift with temperature increased, Diffusion coeffing 1.01 \times 10^{-7} was calculated from Sevcik-Randles equation. Rate constant \( K_{\text{mix}} \) (oxidation) was determined 0.43 \times 10^{-7} and reduction equal 0.31 \times 10^{-7}. The peak current of zinc concentration in the range of 1.0-10.0 ppm showed increased linearly.

Keywords: Cyclic voltammetry; Electrode; ZnO-Nanoparticles; Hydrothermal method

1. Introduction:
Zinc is a trace element and essential for life. [1] Zinc a significance of human nutrition and public health was recognized relatively recently. [2] Zinc insufficiently has been recognized by a number of experts as an important public health issue, especially in developing countries. [3] It's a critical element in body health that even a deficiency is a disaster. [4] Supplementation of zinc is a powerful. [5] Analytical chemistry for quantitative determination of zinc level is significant for immune physiological and pharmacological research. Different type methods applied for the determination of Zn, such as fluorimetry and flow injection [6-8], and optical density methods. [9-11] A modified electrode that common methods using in the electro chemical application because it's has been widely used analytical chemistry methods for sensitive to metals in tiny concentrations in solutions [12-13]. Electrode Surfaces that may be changed with various types of metal. In bio electrochemistry, nanoparticles may be used in a variety of ways. Nanoparticles have electron transfer conduction centers. More types of nanoparticles, have been widely used in electrochemical sensors, such as metal NPs, semiconductor NPs, oxide NPs, and even composite NPs [14]. Zinc is one of the metals can be determined electrochemically because it's electro active component [15]; however, the similar potential and interference cause response signals at bare electrodes transmission are extremely difficult to differentiate. [16] As a result, it's critical to create a new modified electrode that can separate the voltammetric responses. So far, no research on the simultaneous determination of zinc utilizing a carbon paste electrode modified with ZnO-NPs has been published. The production and application of a carbon paste electrode modified with ZnO-NPs electrode
are described in this study. For the first time, a ZnO electrode was used to determine zinc ion in solutions without the need of any extra isolation or precipitation chemicals or particular reagent.

**Zinc oxide** is a crystalline white powder that is water insoluble. Cosmetics, rubbers, ceramics, plastics, glass, cement, food supplements and lubricants are just a few of the materials and products that include it.[16] ZnO belongs to the II-VI semiconductor group and has a large band gap. The semiconductor's native doping is n-type, which is caused by oxygen vacancies or zinc interstitials. [17] Pure ZnO is a white powder, but it is found in nature as the rare mineral zincite, which has a yellow to red color due to manganese and other impurities. [18] At ambient temperature, zinc oxide has a 3.3 eV direct band gap, which is rather high. Higher breakdown voltages, the capacity to tolerate huge electric fields. ZnO's band gap may be further narrowed to 3–4 eV by alloying with MgO or CdO. [17] The electron mobility of ZnO changes dramatically with temperature, peaking at 2000 cm²/(Vs) at 80 K. [19]

2. Materials and methods

Auto Lab Potentiostat (Digi-Ivy 2113 Texas, USA), electrochemical measurements were performed with a controlled by Software electrochemical System. the working electrode is ZnO and ZnO-NPs carbon paste electrode. pH was measured using a metrohm pH/ion meter and a platinum wire as the counter electrode and reference electrode, respectively. All solutions were freshly prepared with distilled water (D.W). All reagents from Merck were of analytical quality, as was paraffin oil and graphite powder. both from Merck were used as received. pure nitrogen gas that used in all solution for deoxygenated. All electrochemical experiments should begin at least 20 minutes before the scheduled start time. The hydro-thermal technique was used to produce ZnO nanoparticles.

ZnO-NPs were produced using a hydrothermal technique. In most cases, 22 g of ZnCl2 was dissolved in 500 mL of D.W., and 2 g of NaOH was added slowly while stirring. After 6 hours, a white precipitate was produced. To achieve a homogenous state, the precipitate was rinsed with distilled water and then combined with 100 mL of (PVP) (10 g of PVP soluble in D.W) a continued stirring solution. The homogenous solution was placed in an autoclave and heated for 16 hours at 160°C. After that, ZnO-NPs powder was produced and dried at 100 degrees Celsius. SEM INSPECT S50 was used to assess the morphology of the produced ZnO-NPs sample. (Figure 1). The ZnO-NPs had an average size of 150 nm, according to the TEM picture.

![Figure 1. TEM image of ZnO nanoparticles.](image-url)
2.1. Preparation of the electrode

0.2 g, 1.2g and 1.0g from ZnO-NPs, graphite powder and paraffin oil; respectively that mix to prepare the ZnO modified carbon paste electrodes Using a mortar and pestle, grind the black paste until it is homogeneous. A glass tube (cross section area 0.3 mm and length 6 cm) Figure 2 and Figure 3 show the structure of ZnO carbon past electrode and ZnO-NPs carbon paste electrode respectively. The mixture was packed into one side of the tube before a copper wire was inserted into the glassy carbon. The graphite paste's surface was polished using fine tissue before the test. Finally, the blank carbon paste electrode was produced using the same conditions as the ZnO carbon paste electrode (ZnO-CPE), but without the addition of ZnO NPs or ZnO to the paste.

Figure 2. The structure of ZnO carbon paste electrode.

Figure 3. The structure of ZnO-NPs carbon paste electrode.
3. Result and Discussion

3.1. A study of zinc using cyclic voltammetry

Cyclic voltametric showed response for the electrochemical oxidation-reduction of 2 ppm and 12 ppm for ZnSO$_4$ solution at ZnO-NPs-CPE and ZnO-CPE; respectfully. the oxidation and reduction peak of Zn$^{2+}$ (-1.461 / -0.770) and (-1.572 / -0.786) refer to ZnO-NPs and ZnO electrodes respectively. Figure 4 showed the voltammograms for the signal redox. While no response was observed on the carbon paste electrode. The result clearly indicated the signal refer to zinc oxidation when combination with graphite powder and ZnO-NPs and ZnO electrodes. The relationship between peak current (Ip) and the square root of scan rate (V$^{1/2}$) was linear in the (0.05) V/s$^{-1}$ range. This implied that, with enough overpotential. [20]

![Figure 4. Cyclic voltammogram of (black) ZnO-NPs-CPE in 2 ppm ZnSO$_4$ solution at the scan rate of 0.1 V/s., (blue) ZnO-CPE in 12 ppm ZnSO$_4$ solution at the scan rate of 0.1 V/s. and (red) refer to the blank electrode.](image)

3.2. Thermodynamic and kinetic parameter determined by temperature study.

A various temperature applied on electrodes was carried out with CV in the range from 10 °C to 40 °C with calomel electrode; the best temperature range 18-25 °C was used for calomel electrode [21]. The activation energy determination by variation of the cyclic voltammogram (j-E) curves Across a wide range of potentials, distinct oxidation peaks occurred. Charge-transfer resistance dependence on temperature, during the electro-oxidation process the rate were constantly connected with a diffusion intermediate's particle size, which was analyzed and discussed, showing that the redox occurred via a complicated mechanism independent of strong contacts with the ZnO-NPs surface of electrode. [22] At 15-30 °C, the working electrode tacked the clear signal using the Nernst equation (Eq.1):

$$\ln D = \ln D_0 - \frac{(E_a)}{RT}$$

(1)

where: $D$ = diffusion coefficient, $T$ = temperature in kelvin.

Slop between ln D and 1/Tk used to calculate of free energy and equal to $E_a = 41.01$ KJ/mol. When voltage was applied to the working electrode, an exothermic process occurred, as shown in Equation (2):

$$\Delta G = -nFR(\Delta Ep)$$

(2)
Where: $\Delta G =$ free energy, $F =$ Faraday constant, $R =$ gas constant, and $E_p =$ difference in potential.

49.7 KJ/mol refer to free Gibb's energy when determined as, this was a reference to the spontaneous reaction According to the previous outcome, Nicholson equation (Eq.3) used to calculate the constant of reaction $K_p$:

$$K = K_0 \exp\left(-\frac{\alpha F}{RT}\right) (E - E_0).$$

(3)

$0.43 \times 10^{-7}$ V/s for the quasi-reversible mechanism refer to first order reaction in cyclic voltammetry. The thermodynamic and kinetic parameters for the ZnO-NPs-CPE and ZnO-CPE are shown in Table 1.

Table 1. Kinetic parameters of ZnO electrodes.

| Type of electrode | $\Delta E$ (KJ/mol) | $\Delta H$ (KJ/mol) | $\Delta G$ (KJ/mol) | $\Delta S$ (KJ/mol) | $K \times 10^{-7}$ | $D^a \times 10^{-7}$ | $A$ | $K_0$ |
|-------------------|---------------------|---------------------|---------------------|---------------------|-------------------|-------------------|-----|-------|
| ZnO-CPE           | 48.12               | 3.79                | 40.3                | 0.297               | 0.31              | 0.89              | 0.1 | 0.14  |
| ZnO-NPs-CPE       | 41.01               | 4.11                | 49.7                | 0.199               | 0.43              | 1.00              | 0.1 | 0.10  |

3.3. Calibration plots and determination of zinc ion

3.3.1. ZnO-NPs-CPE and ZnO-CPE. Cyclic voltammetry was used to identify the quantity of $Zn^{2+}$, as linear ranges of the calibration plots. $Zn^{2+}$ electrochemical response by ZnO-NPs-CPE was investigated. As a result, CV was utilized to determine species simultaneously based on capacitive background current. Analytical experiments were used varying concentrations of ZnSO$_4$ pure stock solution with pH 7.0 by using ZnO-NPs-CPE, obtained at 2-20 ppm, clearly revealing the response the ZnO-NPs-CPE and ZnO-CPE to Zinc ion. Table 2 show the results for sample of zinc that contained vitamins A, C and E, folic acid, lutein, calcium, phosphorus, copper, iron and zinc with composition percentages of 40, 10, 20, 10, 5, 5, 5 and 5%, respectively. Equation (4) was used to prepare the measurement solutions:

$$w.t = \left( \frac{ppm \times wtZn/M \times wtdrug}{10^{-6}} \right) x V$$

(4)

All results pointed out that ZnO-NPs-CPE was more sensitive than ZnO-CPE for determination of trace amount of zinc ion in deferent solutions or drug component.

Table 2. Determined of real stock solution by deferent methods.

| Type of electrode | Analyte (Zn/mg) | Linear range (ppm) | Founded (ppm) | RSD (%) | Theoretical value (ppm) |
|-------------------|-----------------|--------------------|--------------|---------|------------------------|
| ZnO-NPs-CPE       | 2               | $10^3 - 10^3$      | 4.644        | 92.88   | 5                      |
|                   | 4               |                    | 9.198        | 91.98   | 10                     |
|                   | 6               |                    | 14.232       | 94.88   | 15                     |
| ZnO-CPE           | 12              | $10^1 - 10^3$      | 4.102        | 82.04   | 5                      |
|                   | 18              |                    | 8.831        | 88.31   | 10                     |
|                   | 24              |                    | 12.082       | 80.54   | 15                     |

4. Conclusions

Because the increase in surface area perceives tiny changes in the current running through its solution when attached to an electrode surface, ZnO-NPs are more sensitive and selective than ZnO particles. As a result, physical and chemical characteristics are studied. It was used to measure the tiny amounts of zinc metal in several pharmaceutical formulations. When compared to a ZnO carbon past electrode in
sensitive and selective mode, the findings were extremely accurate in reference solutions and actual samples.

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