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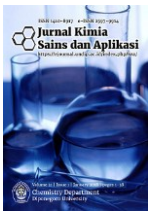

Modification of a Carbon Paste Sensor with TiO_2 and ZnO Nanoparticles for the Cyclic Voltammetric Detection of Retinol

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Abstract

Retinol, a compound belonging to the retinoid group derived from vitamin A, is widely used in cosmetic formulations due to its proven efficacy in skin care. Analytical determination of retinol is commonly performed using conventional techniques such as HPLC and UV-Vis spectrophotometry. An alternative analytical method that offers potential yet remains underexplored is cyclic voltammetry. In this study, a cyclic voltammetry method for retinol analysis was developed using a modified carbon paste working electrode. The modification was done by adding ZnO and TiO_2 nanoparticles to improve the electrode's sensitivity. The sol-gel technique was employed to produce ZnO nanoparticles, which were then analyzed for their characteristics using several instruments, namely XRD, SEM, and FTIR. TiO_2 nanoparticles were also subjected to characterization. The results of the study on ZnO nanoparticle synthesis demonstrated an average particle size measuring 30.5 nm. The optimum electrode composition was obtained at a ratio of 3:2:3:2 (Carbon: ZnO Nanoparticles: TiO_2 Nanoparticles: Paraffin), producing an anodic peak current (IpA) of 4.58×10^{-3} A under optimum pH conditions at pH 7. As the generated peak current increases, the conductivity increases, as electron transfer for the reduction and oxidation processes becomes more facile. Applying this method to retinol analysis in brands X, Y, and Z facial serums yielded retinol contents of 0.00450 ppm, 0.00464 ppm, and 0.00427 ppm. The voltammetric method showed a LoD = 0.001029 ppm and LoQ = 0.003430 ppm, respectively. These results indicate that a ZnO and TiO_2 modified carbon paste electrode is an effective tool for analyzing retinol by cyclic voltammetry.

1. Introduction

The growing desire among the public to enhance beauty, improve appearance, and practice self-care has made cosmetics an essential and integral part of daily life. In response to the increasing demand for cosmetic products, various active ingredients have been developed and diversified to improve both the effectiveness and benefits of these products. All cosmetics marketed to consumers must contain active ingredients that are proven safe for use [1]. One of the active ingredients commonly used in cosmetics is retinol.

Retinol is an active compound belonging to the retinoid group, derived from the weakest and simplest form of vitamin A derivatives, making it safe for use even on sensitive skin [2]. Retinol undergoes oxidative metabolism in the skin to form retinal, which is subsequently oxidized further into retinoic acid [3]. Retinol offers multiple benefits, including slowing and reducing signs of skin aging, preventing and treating acne, stimulating collagen production, reducing pore blockage, and addressing skin hyperpigmentation [4]. The use of retinol in cosmetics is generally permitted by regulatory agencies such as the Indonesian Food and Drug Authority (Badan Pengawas Obat dan Makanan; BPOM) at concentrations of up to 1%; however, the use of retinol at high doses can lead to skin irritation, redness, peeling, and even dryness [5]. Therefore, monitoring retinol levels in cosmetic products is essential to ensure consumer safety and raise awareness regarding its appropriate use.

The concentration of retinol in cosmetic products is typically measured quantitatively using UV-Vis spectrophotometry [6, 7] and High Performance Liquid Chromatography (HPLC) [8, 9]. However, these methods have certain limitations, including relatively high costs, lengthy analysis times, and complex sample preparation procedures [10]. Therefore, it is important to create methods that offer greater efficiency and lower cost with simpler sample preparation and high sensitivity and selectivity for sample detection.

Electrochemical methods such as voltammetry offer an efficient and effective approach for analyzing retinol concentrations. This method is based on measuring the current intensity during electrolysis, which is induced by varying the applied potential over a defined period of time [11]. One commonly used voltammetric technique, and the one employed in this study, is cyclic voltammetry. This technique offers several advantages, including simplicity, stability in oxidizing and reducing over a wide potential range, the ability to analyze analytes at high concentrations, and minimal risk of analyte degradation [12]. Voltammetric instruments typically employ three electrodes: a working electrode, a reference electrode (Ag/AgCl), and an auxiliary electrode (platinum). The working electrode is the site of redox reactions during analysis, and overall, the material chosen for the working electrode greatly impacts the performance of voltammetric methods; as a result, the accuracy and quality of analytical results are largely determined by the choice of working electrode [10, 13].

In this research, the working electrode selected for this study was a carbon paste electrode (CPE) because of its extensive potential window and inert behavior, good electrical conductivity, and ease of application [1, 10]. Despite these advantages, CPE also has notable limitations, including low sensitivity, limited stability, and slow electron transfer kinetics [14]. Therefore, modification materials are needed to increase the electrode's sensitivity, selectivity, and electron transfer kinetics. One promising innovation explored in ongoing research is the incorporation of nanoparticles. Nanoparticles offer a larger surface area, which can improve adsorption capacity on the electrode and enhance its overall performance [15, 16]. Various nanoparticles have been used as CPE modifiers, including gold nanoparticles for uric acid sensors [17], as well as MnO_2, CuO, Fe_2O_3 nanoparticles, zeolite nanoparticles, and nanobentonite, all of which can improve redox reaction capabilities during analysis [1, 18, 19].

In this research, ZnO and TiO_2 nanoparticles were incorporated into the carbon paste electrode. Previous studies by Chikere *et al.* [20] using a ZnO nanoparticle-modified CPE for gallic acid analysis demonstrated a detection limit of 1.86×10^{-7} mol L^{-1} and a sensitivity range of 1.0×10^{-6} mol L^{-1} to 5×10^{-5} mol L^{-1}, indicating that ZnO nanoparticle modification improves detection limits, selectivity, and conductivity when well dispersed on the electrode. Additionally, research by Putri and Setiarso [10] on niacinamide analysis using a TiO_2 nanoparticle-modified CPE with cyclic voltammetry showed enhanced electrode performance, as evidenced by a higher anodic peak current (IpA) of 0.992784 mA compared to the unmodified electrode. The incorporation of these two different nanoparticles is expected to produce synergistic effects that improve electron transfer, thereby achieving high sensitivity, selectivity, and detection limits.

The use of nanomaterials such as TiO_2 and ZnO in the development of electrochemical sensors has been extensively studied due to their semiconducting properties, high surface area, and excellent electron transfer capabilities. However, most studies have focused on the application of these materials individually. The combination of TiO_2 and ZnO forms a type-II heterojunction system, which enhances charge separation and prolongs the lifetime of free charge carriers, thereby improving the sensor's sensitivity and selectivity.

Research on the synergistic effect of these two materials remains limited, particularly for the detection of bioactive compounds such as retinol. Therefore, this study introduces a novel approach by integrating TiO_2 and ZnO nanoparticles into a carbon paste electrode, aiming to improve sensor performance through the synergistic interaction between these two semiconductors. The voltammetric sensor performance for retinol and similar analytes is summarized in Table 1.

In this study, ZnO nanoparticles were obtained through the sol-gel synthesis process, while TiO_2 nanoparticles were obtained commercially. The objective of this study was to propose an alternative method to investigate the effect of incorporating ZnO and TiO_2 nanoparticles as modification materials in carbon paste electrodes for the analysis of retinol levels using cyclic voltammetry. Electrode composition was varied during the analysis to determine the optimal composition and the optimal pH that produced the highest current response in the measurement of retinol concentration.

Table 1. Comparison table of voltammetric sensor performance for retinol or similar analytes

Sensor type and modifier material	Method	Analyte	LoD (ppm)	LoQ (ppm)	Reference
Carbon Paste Electrode (CPE) + TiO_2-ZnO nanoparticles	Cyclic Voltammetry (CV)	Retinol	0.001	0.003	This study
CPE + Surfactant	CV	All-trans retinol	0.14	-	[21]
CPE + TiO_2	CV	Niacinamide	0.342	1.038	[10]
CPE + ZnO	CV	Nicotin	6.78	22.6	[22]

2. Experimental

2.1. Tools and Materials

All reagents were of analytical grade and used as received. Materials included NYA copper wire (4 mm, Kitani), graphite powder (Kimiapedia), paraffin oil, Whatman No. 42 filter paper, NaOH, 1 M HCl, $Na_2HPO_4.H_2O$, $NaH_2PO_4.2H_2O$, distilled water, ethanol (96 %), TiO_2 nanoparticles (anatase, 99.9 %, Labsain), $Zn(CH_3COO)_2.2H_2O$, retinol (99 %, JB Chemical), KCl, a pen tube, and aluminum foil.

The instruments and equipments used in this study included a voltammetry 797 VA, FTIR Thermo Scientific Nicolet iS10, SEM FEI Inspect-S50, XRD X'pert, Eppendorf 5810 centrifuge, Ag/AgCl electrode, beakers, sandpaper, pH meter, Thermo Scientific Cimarec+ magnetic stirrer, Thermo Scientific Precision oven, volumetric flasks, platinum electrode, graduated cylinders, spatulas, Ohaus analytical, dropper pipettes, centrifuge tubes, tongs, burettes, clamps, and a furnace.

2.2. Synthesis of ZnO Nanoparticles

The sol-gel process was employed to synthesize ZnO nanoparticles [22]. $Zn(CH_3COO)_2.2H_2O$ (2 g) was dissolved in 15 mL of distilled water until homogeneous, and NaOH solution was subsequently added dropwise to the zinc acetate mixture until the pH reached 8, while continuously stirring at room temperature until a milky white suspension appeared. Using a burette, 100 mL of 96% ethanol was added dropwise into the suspension. This process resulted in the formation of two distinct phases: a clear liquid and a white precipitate. The precipitate was centrifuged at 5000 rpm for 15 minutes, which was subsequently washed with ethanol and distilled water, oven-dried at 100°C for 30 minutes, and calcined at 500°C for 3 hours [23]. TiO_2 nanoparticles were obtained commercially in nanoparticle form.

2.3. Preparation of ZnO and TiO_2 Nanoparticles-Modified Carbon Paste Electrode

A 15 cm copper wire with a 4 mm diameter was utilized to construct the working electrode. The lower end of the wire was stripped for 0.5 cm, while the other end was stripped for 1.5 cm. The surface of the copper wire was then polished until smooth, even, and shiny. An insulating cover made from a 0.5 mm diameter pen tube, cleaned and cut to a length of 2 cm, was placed on the stripped part of the conductor. The insulating tube served as a holder for the composite carbon paste containing ZnO and TiO_2 nanoparticles.

The electrode paste was prepared by mixing carbon, ZnO nanoparticles, TiO_2 nanoparticles, and paraffin oil. These materials were weighed on an analytical balance using a watch glass, with variations in the ratios of carbon: ZnO nanoparticles: TiO_2 nanoparticles: paraffin as follows: 3:1:4:2, 3:2:3:2, 3:3:2:2, and 3:4:1:2 (w/w). The weighed materials were then mixed in a petri dish until homogeneous. The prepared paste was packed into the copper wire casing and pressed to ensure it was compact. Before being used for analysis, the modified electrode was kept at room temperature for 24 hours.

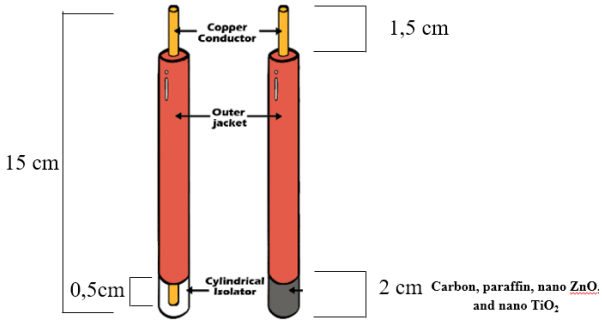

Figure 1. ZnO dan TiO_2 nanoparticles modified for CPE

2.4. Measurement of Optimal Electrode Composition and pH

Electrodes of various compositions were tested using a KCl electrolyte, a phosphate buffer at pH 6, and a standard retinol solution in a voltammetry cell with a scan rate of 0.25 V/s, a potential range from -5 V to 4 V, and a deposition duration of 20 seconds. The optimal electrode was further tested for its optimum pH by varying the pH at 4, 5, 6, 7, and 8. The resulting voltammograms were analyzed using Origin and compared to determine the best composition and the optimum.

2.5. Measurement of Retinol Standard Linearity

The linearity of different standard retinol concentrations was measured using the electrode with optimal composition and conditions to construct a standard curve for retinol at concentrations of 10, 20, 30, 40, and 50 ppm. The resulting voltammograms were used to construct the retinol standard curve.

2.6. Retinol Analysis in Facial Serum Samples

The analysis of facial serum samples was carried out using an electrode with the optimal composition of 3:2:3:2 (w/w) under optimal conditions, utilizing a 5000 ppm KCl electrolyte solution at the optimal pH (pH 5), within a potential range of -5 V to 4 V, with an optimal deposition time of 20 seconds and an optimal scan rate of 0.25 V/ms, using the cyclic voltammetry method.

3. Results and Discussion

3.1. Synthesis and Characterization of ZnO Nanoparticles

This study utilized a bottom-up synthesis route for ZnO nanoparticles via the sol-gel method [22]. This method was selected because it allows synthesis at relatively low heating temperatures, providing control over particle size and morphology [24]. $Zn(CH_3COO)_2.2H_2O$ was used as the precursor. The use of this precursor facilitates precise control of nanoparticle dimensions, leading to consistent particle size and minimal clumping, and then allows for the formation of uniform particle morphology during the hydrolysis and condensation processes [24, 25]. The reaction mechanism involved in the synthesis of ZnO nanoparticles includes hydrolysis as described in Equation (1), condensation as shown in Equation (2), and the aging process outlined in Equation (3).

$$Zn(CH_3COO)_2.2H_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}{}_{(aq)} + 2CH_3COO^-{}_{(aq)} + 2H_2O_{(l)} \quad (1)$$

$$Zn^{2+}{}_{(aq)} + 2CH_3COO^-{}_{(aq)} + 2Na^+{}_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + 2CH_3COONa_{(aq)} + 2H^+{}_{(aq)} \quad (2)$$

$$Zn(OH)_{2(aq)} \rightarrow ZnO_{nps} + H_2O \quad (3)$$

The synthesized ZnO nanoparticles were then characterized using XRD, FTIR, and SEM techniques. FTIR spectroscopy was employed to identify functional groups formed during the sol-gel synthesis, with measurements taken in the 400–4000 cm^{-1} range. Based on Figure 2 and Table 2, the relatively weak absorption band at the peak of 3368.00 cm^{-1} indicates the symmetric stretching vibration of the O-H group forming hydrogen bonds. The wave number at 1373.09 cm^{-1} corresponds to the stretching vibration of C-O from the alcohol molecule C- OH. The wave number at 866.94 cm^{-1} indicates the stretching vibration of Zn-O. This FTIR spectrum confirms that the ZnO structure has been formed.

XRD analysis was utilized to identify the material's crystalline phases, evaluate its lattice structure, and measure the crystallinity and particle size. The ZnO nanoparticles were characterized using XRD at a scan rate of 5–90° with an X-ray wavelength of 1.54060 Å. The diffraction pattern, shown in Figure 3, displays sharp peaks at 2θ angles of 31.8494°, 34.4795°, 36.4112°, 47.6788°, 56.6920°, 62.9788°, 66.4538°, and 69.1770°, which correspond to the (hkl) planes of the wurtzite hexagonal ZnO structure. The highest peak appears at 2θ = 36.4112°, with a relative intensity of 100%. Table 3 indicates that the mean crystallite size of the ZnO nanoparticles is 30.556215 nm. Nanoparticles are generally considered to be particles ranging from 1 to 100 nm in size [1].

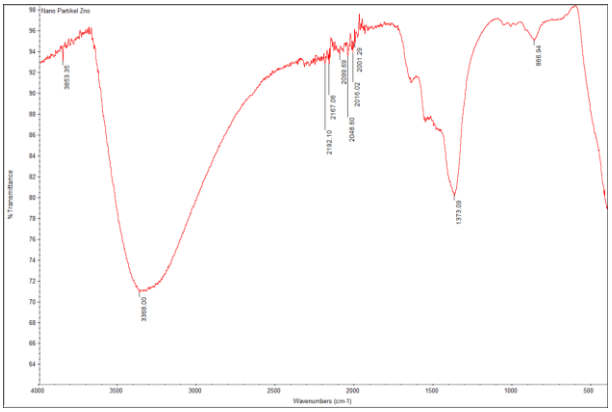

Figure 2. FTIR spectrum of ZnO nanoparticles

Table 2. Functional groups and corresponding FTIR wavenumbers of ZnO nanoparticles

Functional group	Wavenumbers (cm^{-1})		
	Research data	Reference	Source
O-H	3368.00	3000–3900	Sharma and Garg [26]
C-O	1373.09	1300–1400	Sharma and Garg [26]
Zn-O	866.94	701–1033	Bashir *et al.* [27]

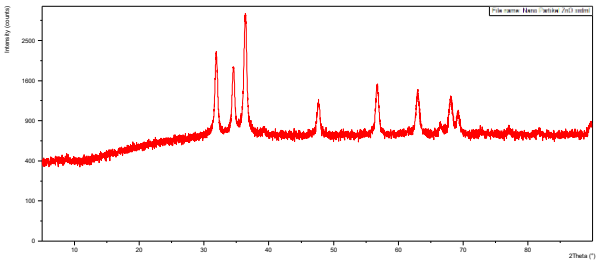

Figure 3. XRD pattern of ZnO nanoparticles

XRD analysis not only identifies the crystal structure and phases of the synthesized material but also allows for estimating the crystal size. This estimation is performed using the Debye-Scherrer equation, which is a common method for calculating the size of crystalline domains based on the broadening of diffraction peaks. The Debye-Scherrer equation incorporates the full width at half maximum (FWHM) of the diffraction peaks and the X-ray wavelength, as demonstrated in Equation (4).

$$D = \frac{K\,\lambda}{\beta \cos\theta} \quad (4)$$

Where, D is the crystallite (particle) size in nanometers (nm), K is the shape factor of the crystal (typically 0.89), λ is the wavelength of the X-ray (1.5406 Å or 0.15406 nm), β is the Full Width at Half Maximum (FWHM) of the diffraction peak in radians, and θ is the angle of diffraction (Bragg angle) in radians.

SEM was employed for additional physical characterization to observe the morphology of the synthesized ZnO nanoparticles. As shown in Figure 4, the particles exhibit a spherical shape and a non-uniform size distribution. The average particle size, calculated using ImageJ software, is 41.88 nm. This result indicates that the ZnO compound synthesized via the sol-gel method has a nanoparticle structure, as it falls within the size range of 1–100 nm [22].

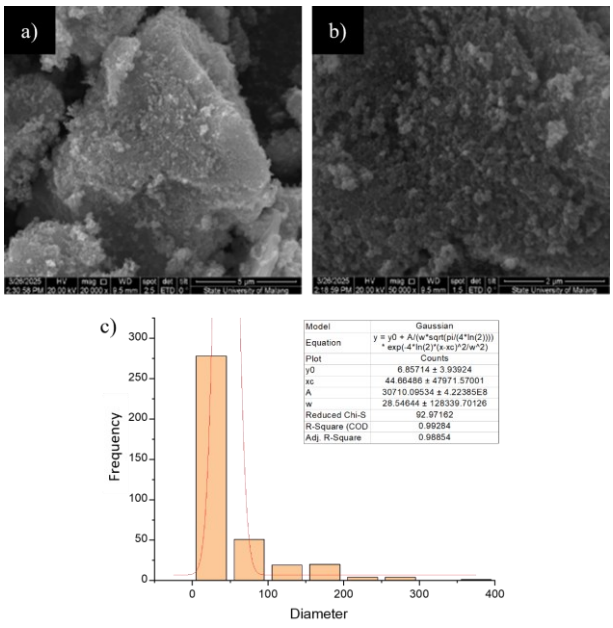

Figure 4. (a) SEM micrograph of ZnO nanoparticles with 20,000× magnification, (b) SEM micrograph of ZnO nanoparticles with 50,000× magnification, (c) calculation result of ZnO diameter

Table 3. XRD diffraction peaks and corresponding crystallite sizes of ZnO nanoparticles

Pos. (°2Th.)	FWHM left (°2Th.)	d-spacing (Å)	Crystal size (nm)
31.8494	0.1171	2.80981	70.54939
34.4795	0.1338	2.60126	62.16735
36.4112	0.3680	2.46757	22.72534
39.1764	0.8029	2.29954	10.5023
47.6788	0.2676	1.90744	32.45629
56.6920	0.2676	1.62373	33.73173
62.9788	0.3011	1.47593	30.94064
66.4538	0.4015	1.40693	23.65374
68.0152	0.4015	1.37839	23.869
69.1770	0.4015	1.35805	24.03464
77.0378	0.5353	1.23791	18.96826
81.6529	0.8029	1.17922	13.07596

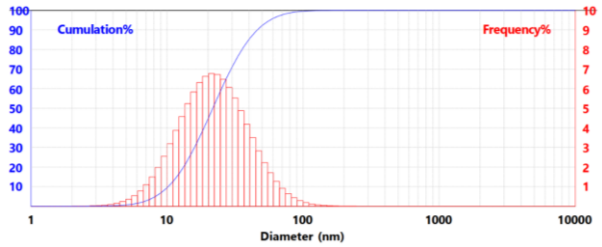

Figure 5. Particle size distribution graph of TiO_2 nanoparticles

3.2. Characterization of TiO_2

The characterization of TiO_2 nanoparticles was carried out using a Particle Size Analyzer (PSA) to confirm that the directly purchased TiO_2 nanoparticles fall within the nanometer size range of 1–100 nm. The PSA analysis results showed that the TiO_2 nanoparticles had an average particle size of 38.34 nm, with D10, D50, and D90 values of 10.19 nm, 21.69 nm, and 46.21 nm, respectively. These results demonstrate that the majority of particles are within the nanometer scale. The detailed results are presented in Figure 5.

In addition to PSA, the morphological structure of the TiO_2 nanoparticle surface was characterized using SEM at magnifications of 20,000× and 50,000×, as shown in Figure 6. The SEM images reveal that the surface morphology tends to be spherical and rough, indicating good interconnection between particles with a relatively uniform particle size distribution.

3.2.1. Determination of the Optimum ZnO Nanoparticles and TiO_2 Nanoparticles Electrode Composition

To identify the best formulation, the peak current produced by each composition of the ZnO and TiO_2 nanoparticle-modified CPE was measured using a 50 ppm standard retinol solution at pH 6, measured by cyclic voltammetry over a potential range of -5 V to +4 V. The tested composition ratios of carbon: ZnO nanoparticles: TiO_2 nanoparticles: paraffin were 3:1:4:2, 3:2:3:2, 3:3:2:2, and 3:4:1:2 (w/w), respectively.

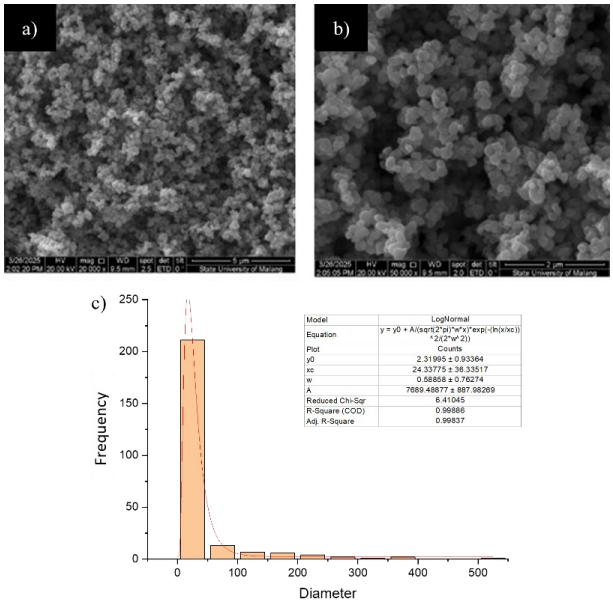

Figure 6. SEM images of TiO_2 nanoparticles at (a) 20,000×, (b) 50,000× magnification. (c) calculation result of TiO_2 anatase diameter

3.2.2. Determination of the Optimum ZnO Nanoparticles and TiO_2 Nanoparticles Electrode Composition

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Carbon, ZnO nanoparticles, and TiO_2 nanoparticles function as conductors that facilitate electrical conductivity within the composite. Paraffin serves as a binder to hold the modified CPE together and acts as a hydrophobic agent to prevent further solution penetration into the electrode, thereby minimizing electrode damage.

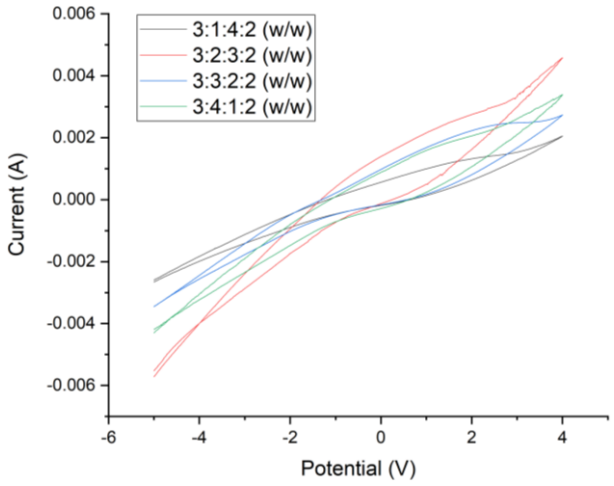

Figure 7. Voltammogram of CPE modified with varying compositions of ZnO and TiO_2 nanoparticles

Retinol is highly susceptible to oxidation under electrochemical conditions. The presence of an oxidation (anodic) peak current in the voltammogram signifies this behavior. Conversely, the reduction is less efficient, resulting in a relatively small current. The observed phenomenon can be explained by a sluggish charge transfer rate or a rapid homogeneous reaction of the oxidation product. In other words, the electrochemical reaction of retinol is irreversible because a single anodic peak (oxidation) with no corresponding cathodic peak (reduction) on the reverse scan [28].

The ease of retinol oxidation is attributed to the presence of a hydroxyl group (-OH) at the end of the β-ionone ring and a polyisoprenoid chain with conjugated double bonds, which makes the molecule prone to electron loss (oxidation). The oxidation process of retinol is illustrated in Figure 9. Meanwhile, Figure 7 shows that the peak current varies depending on the composition of the working electrode used, indicating that these electrodes exhibit selectivity in detecting retinol.

Table 4. Peak currents of CPE modified with ZnO and TiO_2 nanoparticles

Composition (w/w)	IpA (A) ($\times 10^{-3}$)
3:1:4:2	3.52
3:2:3:2	4.58
3:3:2:2	2.72
3:4:1:2	3.39

Table 5. Peak current values for modified and unmodified working electrodes

Composition (w/w)	IpA (A) ($\times 10^{-3}$)
8:2	2.94
3:5:2 (NZ)	2.60
3:5:2 (NT)	1.19
3:2:3:2	4.58

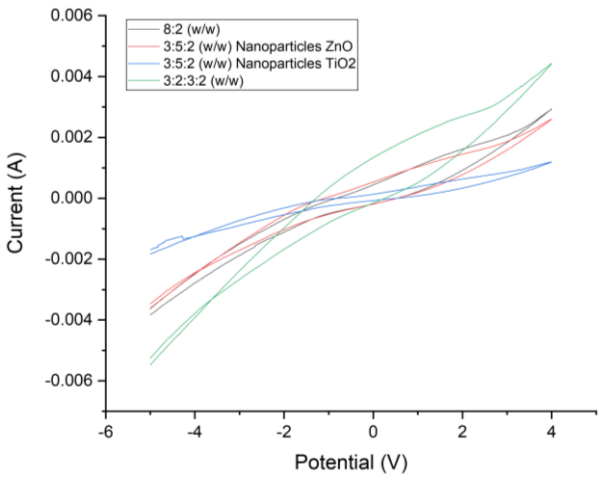

Figure 8. Voltammograms of modified and unmodified working electrodes

Table 4 shows that the highest IpA value of 4.58×10^{-3} A was achieved at the composition ratio of 3:2:3:2 (w/w). A higher peak current indicates better electrode conductivity through enhanced electron transfer during the redox process [12]. The oxidation peak can be identified using Origin 2028 software with the Data Reader tool.

The modification of the working electrode significantly affects the resulting peak current. The CPE with paraffin without nanoparticles produced a curve that tended to be symmetric, while the electrode modified with ZnO nanoparticles showed a slight improvement compared to the unmodified one. In contrast, the electrode modified with TiO_2 nanoparticles generated relatively low currents, even lower than those of ZnO. However, combining ZnO and TiO_2 nanoparticles in the CPE significantly increased the peak current.

The increase in the IpA value on the modified electrode with ZnO nanoparticles and TiO_2 nanoparticles for CPE shows an improvement compared to the unmodified electrode. It can be proven that electrode modification can result in new properties that enhance the absorption of the retinol sample or improve electron transfer, thus providing better electrochemical performance.

3.2.3. Determination of Optimum pH

After determining the optimal electrode composition, the next step was to determine the optimal pH to prevent electrode surface instability from ongoing reactions. Since redox potential varies with pH, a range of 4 to 8 was tested using a 0.1 M phosphate buffer to maintain a consistent pH. This range was chosen because retinol is most stable between pH 5 and 7, which favors oxidation [29]. Figure 10 shows the voltammogram at the optimal pH, and Table 5 provides the corresponding peak currents.

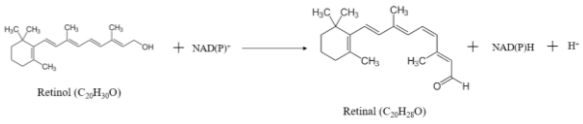

Figure 9. Oxidation reaction of retinol

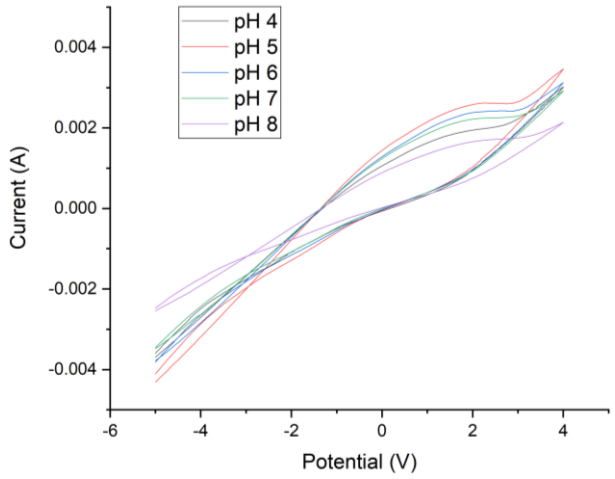

Figure 10. Voltammogram of pH variation

Based on Figure 10, there is no significant comparison of peak currents at each pH variation; however, pH still influences the increase in IpA. The use of phosphate buffer can affect the test solution, as it can enhance the conductivity of the solution and maintain a constant ionic strength [10].

Based on Table 6, the measurement results show that at pH 5, the retinol solution undergoes oxidation, which is the optimum pH. The extent of oxidation can be proven by the IpA value of 3.46 × 10^{-3}. A for the retinol measurement, as under these conditions, retinol remains stable and ionizes optimally at pH 5. The higher the peak current value generated in the retinol analysis across different pH variations, the higher the electron transfer [20]. As the peak current increases, the analysis of the test solution concentration can be performed, as the measured concentration is linearly related to the measured current.

3.2.4. Measurement of Standard Retinol Linearity

The purpose of measuring the linearity of retinol standard solutions was to confirm the capability of the instrument or method to generate consistent and linear responses over a range of concentrations. Specifically, cyclic voltammetry could deliver reliable and precise results when determining retinol concentrations, especially within a defined linear concentration range. Experiments were performed with the electrode composition and pH set at their optimal values. Voltammogram data for the different concentrations of retinol standard solutions are shown in Figure 11.

Table 6. Peak currents at different pH values

pH	IpA (A) (× 10^{-3})
4	3.02
5	3.46
6	3.12
7	2.92
8	2.13

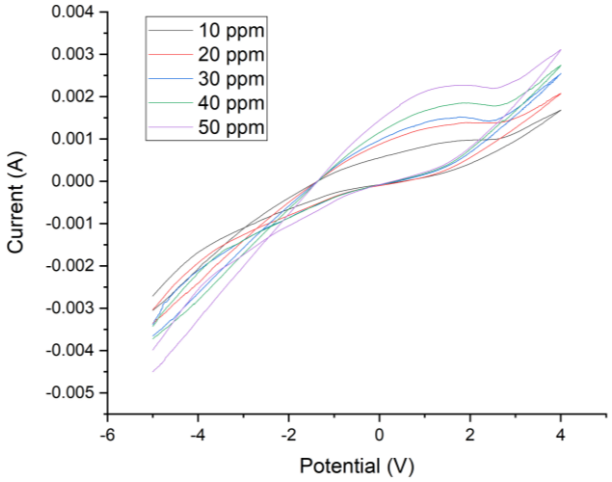

Figure 11. Voltammogram of standard retinol solution

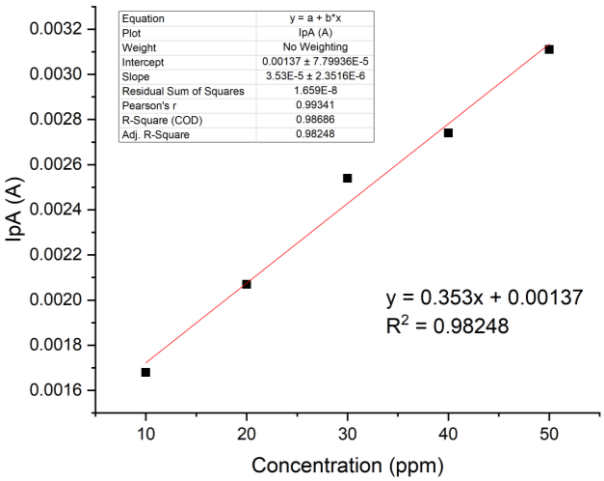

Figure 12. Linear calibration curve of retinol standard solution

As depicted in Figure 11, the voltammogram of the retinol standard displays a linear trend, suggesting a direct correlation between the concentration of the standard solution and the peak current, with higher concentrations leading to a higher peak current. Table 7 shows the IpA values for the retinol standard solutions at different concentrations.

Figure 12 shows a clear linear relationship between retinol concentration and its oxidation peak current, described by the equation y = 0.353x + 0.00137, where the slope (a) is 0.353 and the intercept (b) is 0.00137. The fit quality is high, with an adjusted R^2 of 0.98248. This equation was used to determine unknown retinol concentrations via cyclic voltammetry.

Table 7. Peak current of the standard retinol solution

Concentration (ppm)	IpA (× 10^{-3})
10	1.68
20	2.07
30	2.54
40	2.74
50	3.11

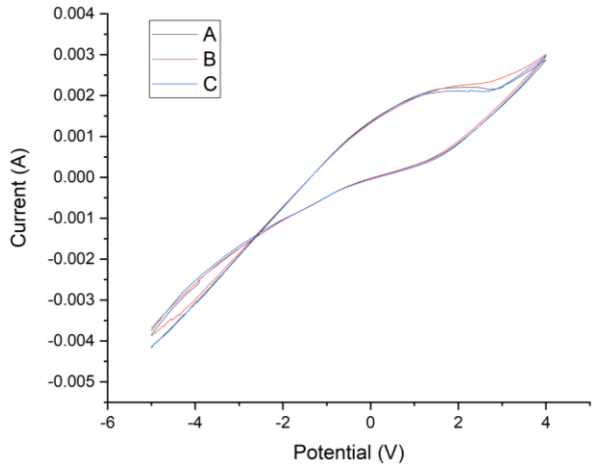

Figure 13. Voltammogram of the retinol solution in the product

Table 8. Peak Current of the retinol solution in the product

Sample	IpA (A) (× 10^{-3})	Concentration (ppm)
X	2.96	0.00450
Y	3.01	0.00464
Z	2.88	0.00427

3.2.5. Limit of Detection and Limit of Quantification

$$LoD = \frac{3 \times s\left(\frac{y}{x}\right)}{slope}$$

LoD = 0.001029 ppm

$$LoQ = \frac{10 \times s\left(\frac{y}{x}\right)}{slope}$$

LoQ = 0.003430 ppm

3.2.6. Testing of Retinol in Facial Serum Samples

The retinol concentration was measured in three commonly available facial serum samples. The voltammogram data for the facial serum sample solution are shown in Figure 13. By substituting the IpA from the cyclic voltammetry results into the standard curve equation, y = 0.353x + 0.00137, the retinol concentration in the facial serum sample can be calculated. The three retinol serum samples showed similar curve shapes with slight differences in current, which may indicate differences in concentration or interactions between the serum matrix and retinol. Based on the data in Table 8, the three samples showed relatively similar retinol concentrations, ranging from 0.00427 to 0.00464 ppm. This suggests that the serum formulations have a consistent retinol content. The cyclic voltammetry method has proven to be effective and sensitive for detecting retinol at low concentrations and is highly relevant for sensor applications in cosmetic testing.

4. Conclusion

A composition of 3:2:3:2 (carbon: ZnO nanoparticles: TiO_2 nanoparticles: paraffin) in the modification of carbon paste electrodes provides the best peak current for identifying retinol solution. The best measurement conditions for retinol analysis using cyclic voltammetry are at pH 5, with an IpA value of 3.46 × 10^{-3} A. The retinol content obtained through cyclic voltammetry for facial serum samples from brands X, Y, and Z was 0.00450, 0.00464, and 0.00427 ppm, respectively. The voltammetric method showed a LoD = 0.001029 ppm and LoQ = 0.003430 ppm. These results indicate that the CPE modified with ZnO and TiO_2 nanoparticles, combined with cyclic voltammetry, can be effectively used for retinol analysis.

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References

[1] Ahmad Jihad Hizbullah, Pirim Setiarso, Fabrication of Carbon Paste Electrode Modified with Bentonite Nanoparticles and Titanium Dioxide Nanoparticles for Analysis of Methyl Parabens by Cyclic Voltammetry, *Jurnal Pijar Mipa*, 19, 1, (2024), 119-124 https://doi.org/10.29303/jpm.v19i1.5949

[2] Tania Salsabila Putri Harfi, Neneng Siti Silfi Ambarwati, Pembuatan buku saku panduan pemakaian retinol untuk mencegah penuaan bagi pemula, *Jurnal Tata Rias*, 12, 2, (2022), 43-53 https://doi.org/10.21009/jtr.12.2.05

[3] Jeffrey J. Yourick, Connie T. Jung, Robert L. Bronaugh, In vitro and in vivo percutaneous absorption of retinol from cosmetic formulations: Significance of the skin reservoir and prediction of systemic absorption, *Toxicology and Applied Pharmacology*, 231, 1, (2008), 117-121 https://doi.org/10.1016/j.taap.2008.04.006

[4] Putri Wulan Birru, Indah Laily Hilmi, Salman Salman, Article Review : Retinol In Cosmetics, *Journal of Pharmaceutical and Sciences*, 6, 1, (2023), 256-260 https://doi.org/10.36490/journal-jps.com.v6i1.15

[5] Yohanes Firmansyah, Sukmawati Tansil Tan, Brief and Evidence Review: Kombinasi Tretinoin, Klindamisin, dan Dexamethasone Topikal untuk Terapi Acne Vulgaris, *Jurnal Medika Hutama*, 3, 02 Januari, (2022), 2400-2447

[6] Nurillahi Febria Leswana, Clara Ritawany Sinaga, Identification Retinoic Acid Content in Online Whitening Cream Sold in Samarinda City Using Thin Layer Chromatography (TLC) and Spectrophotometry UV-Visible Methods, *Journal of Pharmaceutical and Sciences*, 5, 2, (2022), 174-180 https://doi.org/10.36490/journal-jps.com.v5i2.112

[7] Fendi Yoga Wardana, Yunida Senja Lestari, Rakhmadani Gadis Aprilianti, Analysis of Retinoic Acid Content on Night Whitening Cosmetic Cream in Malang City, *PHARMADEMICA : Jurnal Kefarmasian dan Gizi*, 1, 2, (2022), 58-68 https://doi.org/10.54445/pharmademica.v1i2.17

[8] Baitha Palanggatan Maggadani, Risa Rahmayati, Taufiq Indra Rukmana, Callista Andinie Mulyadi, Retinol Stability in Anti-Aging Face Serum Post-

Opening Period, *International Journal of Applied Pharmaceutics*, 16, 4, (2024), 108-113 https://doi.org/10.22159/ijap.2024v16i4.50903

[9] Satoshi Yokota, Shigeru Oshio, A simple and robust quantitative analysis of retinol and retinyl palmitate using a liquid chromatographic isocratic method, *Journal of Food and Drug Analysis*, 26, 2, (2018), 504-511 https://doi.org/10.1016/j.jfda.2017.07.002

[10] Dhea Anggraini Putri, Pirim Setiarso, Fabrication of carbon pasta elektroda composition modified with nanobentonite and nano TiO_2 for niacinamide detection sensor, *Jurnal Pijar Mipa*, 18, 6, (2023), 923-928 https://doi.org/10.29303/jpm.v18i6.5847

[11] Javier Ernesto Vilasó Cadre, Alejandro Céspedes Martínez, María de los Ángeles Arada Pérez, José Alejandro Baeza Reyes, Voltammetric method for the quantification of cadmium using non-commercial electrodes and minimal instrumentation, *Eclética Química*, 44, 1, (2019), 53-61 https://doi.org/10.26850/1678-4618eqj.v44.1.2019.p53-61

[12] Noémie Elgrishi, Kelley J. Rountree, Brian D. McCarthy, Eric S. Rountree, Thomas T. Eisenhart, Jillian L. Dempsey, A Practical Beginner's Guide to Cyclic Voltammetry, *Journal of Chemical Education*, 95, 2, (2018), 197-206 https://doi.org/10.1021/acs.jchemed.7b00361

[13] Nerry Puspita Sari, Pirim Setiarso, Pembuatan Elektroda Kerja *Graphene Oxide* Termodifikasi Nano Bentonit Untuk Analisis Asam Nikotinat Secara Voltametri Siklik, *UNESA Journal of Chemistry*, 9, 3, (2020), 170-178 https://doi.org/10.26740/ujc.v9n3.p170-178

[14] Somayeh Tajik, Hadi Beitollahi, Fariba Garkani Nejad, Mohadeseh Safaei, Kaiqiang Zhang, Quyet Van Le, Rajender S. Varma, Ho Won Jang, Mohammadreza Shokouhimehr, Developments and applications of nanomaterial-based carbon paste electrodes, *RSC Advances*, 10, 36, (2020), 21561-21581 https://doi.org/10.1039/d0ra03672b

[15] Antonella Curulli, Nanomaterials in Electrochemical Sensing Area: Applications and Challenges in Food Analysis, *Molecules*, 25, 23, (2020), 5759 https://doi.org/10.3390/molecules25235759

[16] Jaclyn E. Kellon, Samantha L. Young, James E. Hutchison, Engineering the Nanoparticle–Electrode Interface, *Chemistry of Materials*, 31, 8, (2019), 2685-2701 https://doi.org/10.1021/acs.chemmater.8b04977

[17] Muji Harsini, Bernadeta Ayu Widyaningrum, Erna Fitriany, Denok Risky Ayu Paramita, Ainiy Nur Farida, Afaf Baktir, Fredy Kurniawan, Satya Candra Wibawa Sakti, Electrochemical synthesis of polymelamine/gold nanoparticle modified carbon paste electrode as voltammetric sensor of dopamine, *Chinese Journal of Analytical Chemistry*, 50, 4, (2022), 100052 https://doi.org/10.1016/j.cjac.2022.100052

[18] Emad Salaam Abood, Ahmed Salim Abed, Zahara Njah Salman, New Fe_2O_3 Nanoparticles Modified Carbon Paste Electrode: A Cyclic Voltammetric Study, *Egyptian Journal of Chemistry*, 64, 12, (2021), 7509-7515 https://doi.org/10.21608/ejchem.2021.100563.4672

[19] Amardi Suprasetyo, Pirim Setiarso, Pembuatan elektroda pasta karbon termodifikasi zeolit untuk analisis fenol secara *cyclic stripping voltammetry*, *UNESA Journal of Chemistry*, 5, 3, (2016), 86-93

[20] C. Chikere, N. H. Faisal, P. K. T. Lin, C. Fernandez, Zinc oxide nanoparticles modified-carbon paste electrode used for the electrochemical determination of Gallic acid, *Journal of Physics: Conference Series*, 1310, 1, (2019), 012008 https://doi.org/10.1088/1742-6596/1310/1/012008

[21] Simona Žabčíková, Tomáš Mikysek Mikysek, Libor Červenka, Milan Sýs, Electrochemical Study and Determination of All-*trans*-Retinol at Carbon Paste Electrode Modified by a Surfactant, *Food technology and biotechnology*, 56, 3, (2018), 337-343 https://doi.org/10.17113/ftb.56.03.18.5618

[22] Vita Ayu Fatihah, Pirim Setiarso, The Fabrication of ZnO Nanoparticles-Modified Carbon Paste Electrode for the Analysis of Nicotine Content in E-Cigarette Liquids by Cyclic Voltammetry, *Indonesian Journal of Chemical Research*, 12, 2, (2024), 104-112 https://doi.org/10.30598/ijcr.2024.12-vit

[23] Gunja Singh, Satya Pal Singh, Synthesis of zinc oxide by sol-gel method and to study it's structural properties, *AIP Conference Proceedings*, 2220, 1, (2020), 020184 https://doi.org/10.1063/5.0001593

[24] Choiry Ghina Afrilia, Annisa Aprilia, Lusi Safriani, Ayi Bahtiar, Davi Putri Hanavi, Studi proses sintesis serbuk nano ZnO beserta karakterisasi, *JIIF (JurnalIlmu dan InovasiFisika)*, 3, 2, (2019), 105-113 https://doi.org/10.24198/jiif.v3i2.23063

[25] Maria-Anna Gatou, Nefeli Lagopati, Ioanna-Aglaia Vagena, Maria Gazouli, Evangelia A. Pavlatou, ZnO Nanoparticles from Different Precursors and Their Photocatalytic Potential for Biomedical Use, *Nanomaterials*, 13, 1, (2023), 122 https://doi.org/10.3390/nano13010122

[26] Tamanna Sharma, Maneesha Garg, Optical and morphological characterization of ZnO nano-sized powder synthesized using single step sol-gel technique, *Optical Materials*, 132, (2022), 112794 https://doi.org/10.1016/j.optmat.2022.112794

[27] Saiqa Bashir, Muhammad Siddique Awan, Muhammad Akhyar Farrukh, Ravi Naidu, Shahzad Akbar Khan, Nagina Rafique, Shaista Ali, Imran Hayat, Imtiaz Hussain, Muhammad Zubair Khan, In-vivo (*Albino Mice*) and in-vitro assimilation and toxicity of zinc oxide nanoparticles in food materials, *International Journal of Nanomedicine*, 2022, 17, (2022), 4073-4085 https://doi.org/10.2147/IJN.S372343

[28] Nadia Ait Ahmed, Houa Hammache, Marielle Eyraud, Carine Chassigneux, Florence Vacandio, Philippe Knauth, Laid Makhloufi, Nour-eddine Gabouze, Voltammetric determination of ascorbic acid with zinc oxide modified glassy carbon electrode, *Journal of the Iranian Chemical Society*, 16, 9, (2019), 1957-1963 https://doi.org/10.1007/s13738-019-01668-5

[29] M. E. Carlotti, V. Rossatto, M. Gallarate, M. Trotta, F. Debernardi, Vitamin A palmitate photostability and stability over time, *International Journal of Cosmetic Science*, 26, 5, (2004), 270-270 https://doi.org/10.1111/j.1467-2494.2004.00233_1.x