Preparation of GCE modified with ZnO@CoFe$_2$O$_4$ magnetic nanoparticles and its application in electrocatalytic determination of Acetaminophen

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In this work, a nanocomposite of zinc oxide (ZnO) and cobalt ferrite (CoFe$_2$O$_4$) was synthesised with a facile preparation method in order to fabricate a nanosensor for acetaminophen (AC) sensing. The ZnO nanoparticles were electrochemically deposited onto glassy carbon electrode (GCE) coated with magnetic nanoparticles CoFe$_2$O$_4$. The morphology and structure of ZnO@CoFe$_2$O$_4$ nanocomposite were investigated by scanning electron microscopy and energy dispersive X-ray. The performance of the proposed sensor was characterised with cyclic voltammetry and differential pulse-voltammetry techniques. The ZnO@CoFe$_2$O$_4$/GCE nanosensor shows excellent electrocatalytic activity for AC oxidation in phosphate buffer (pH = 7) solution and it exhibits a good linear relationship and the low limit of detection (LOD). The ZnO@CoFe$_2$O$_4$/GCE showed good sensitivity, selectivity, stability, reproducibility, larger specific area and fast response in comparison with other reported sensors. The result calibration diagram of using the differential pulse-voltammetric technique has two linear ranges of 0.495–9.53 and 9.53–47.00 μm, and the LOD for AC by this method obtained 0.36 μm. The performance of this modified electrode was evaluated for measuring AC in some pharmaceutical formulations.

1. Introduction: Acetaminophen (AC) (or N-acetyl-amino-phenol) application as an analgesic and antipyretic drug has been extensively used for relief of pains or for reduction of fevers [1, 2]. This drug is an effective and secure analgesic agent that is applied to reduce mild to moderate pain including headache, muscular aches, arthritis, post-surgical and cancer pain [2]. However, AC produces toxic metabolites through metabolism in the liver. Overdose consumption of AC can induce accumulation of toxic metabolites, causing fatal liver harm [3, 4]. Therefore, it is necessary to determine the concentration of AC in drug and biological samples. AC has been analysed using various methods including electrochemical techniques [1–15], liquid chromatograph [16, 17] and spectrophotometry [18–20]. Since AC is an electroactive substance, electrochemical methods are more efficient compared with other methods because of their simplicity and ease of use, as well as no need for complicated separation methods and time-consuming preparation. As of today, several kinds of modified electrodes with nanoparticles such as glassy carbon electrode (GCE) modified with iron sulphide and reduced graphene oxide (FeS/rGO) nanosheets [1], Nanostructured hexacyanoferrate intercalated nickel–aluminium (Ni–Al) layered double hydroxide modified electrode [2], GCE based on electrochemically reduced graphene (ERG) loaded Ni oxides (Ni$_2$O$_3$–NiO) nanoparticles (ERG/Ni$_2$O$_3$–NiO/GCE) [3], GCE modified with titanium dioxide (TiO$_2$) [5], graphene/cobalt ferrite (CoFe$_2$O$_4$) nancomposite modified carbon paste electrode [6], GCE modified with CoFe$_2$O$_4$ [7], carbon paste electrode modified with hydroquinone derivative and graphene oxide nanosheets [8], GCE modified with nafion/ruthenium oxide pyrochlore [9], GCE modified with complexation of copper (Cu) ions in a terthiophene carboxylic acid (TTCA) polymer film [10], the polyaniline wrapped–multi-walled carbon nanotubes (CNTs) composite-based electrode [11], GCE modified with carbon-coated Ni magnetic nanoparticles [12] and bismuth oxide nanorod modified screen printed [13] have been used in order to measure AC.

Magnetic nanoparticles are the subject of many scientists' research, considering their application in various fields of technology including permanent magnets, microwave devices and high-density data storage. Among the magnetic nanoparticles, CoFe$_2$O$_4$ has been very much considered due to its excellent chemical stability, mechanical hardness, high electromagnetic performance, environmental compatibility, electrocatalytic activity and its successful applications in electrochemicals due to controllable crystalline size of this nanoparticle. CoFe$_2$O$_4$ nanoparticles were synthesised by various methods including mechano-synthesis [21] and chemical synthesis [6, 7, 22–24]. In these articles, nanoparticle CoFe$_2$O$_4$ and its nanocomposites are used as electrode modifier for measuring various electroactive materials.

Zinc oxide (ZnO) is one of the richest nanostructures in electrochemical fields. In recent years, nanostructures have attracted considerable attention in applications of electrical and photovoltaic. ZnO has three features: first, that it is the semiconductor with a wide bandgap of 37.3 eV and large exciton binding energy of 60 meV. Its second feature is its piezoelectricity, which is very useful in sensors. Finally, its third feature is expressed as it is biocompatible and safe, which can be easily applied in medical applications [25]. In literatures [26–29], nanoparticle ZnO and its nanocomposites are used as electrode modifier for measuring various electroactive materials.

In this Letter, we offer a facile and successful preparation method for synthesis of ZnO@CoFe$_2$O$_4$ magnetic nanoparticles in order to fabricate a nanosensor for AC sensing. This electrochemical sensor is suggested for determination of AC with satisfactory results, which suggests the practical applicability of the sensor. The proposed sensor benefits the advantages such as highly repeatable, has good detection of limit and good linear range, and it is also an inexpensive and facile method.

2. Experimental results
2.1. Apparatus and instruments: For electrochemical measurements, a PGSTAT 20 Autolab potentiostat from ECO Chemie (The Netherlands) was utilised. An electrochemical cell with a conventional three-electrode system was used, which included a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the auxiliary electrode and modified GCE as the working electrode. All electrodes were obtained from Azar Electrode Co., Urmia, Iran. The pH values of solutions were determined using a Metrohm 827 pH meter (Switzerland Metrohm Company). To study the structure and morphology of the nanoparticles, scanning electron microscopy (SEM) and MIRA3 TESCAN energy dispersive X-ray (EDX) were utilised.

2.2. Materials: All Materials and reagents used in this work were of analytical grade. Utilised chemicals in order to synthesise nanoparticles in this work are zinc nitrate tetrahydrate [$Zn(NO_3)_2.4H_2O$], potassium nitrate (KNO_3), cobalt(II) chloride tetrahydrate ($CoCl_2.4H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$) and sodium hydroxide (NaOH). Potassium hexacyanoferrate (II) [$K_4Fe(CN)_6$] and potassium chloride (KCl) were used to calculate the electrode surface. Phosphoric acid, sodium dihydrogen phosphate dihydrate, HCl and NaOH were used to prepare phosphate buffer. All of these chemicals were prepared from Merck (Germany). The solutions were prepared with double distilled water. Medicinal samples were obtained from Amin and Abidi Companies (Tehran, Iran).

2.3. Chemical synthesis of $CoFe_2O_4$: The $CoFe_2O_4$ nanoparticles were synthesised approximately as described in [22]. Briefly, 0.1080 g of $FeCl_3.6H2O$ salt and 0.0485 g of $CoCl_2.4H_2O$ salt were dissolved in 50 ml distilled water. About 10 ml of NaOH (6 M) solution was dropwise added to the reaction mixture. Resulting solution was refluxed at 100°C for 8 h. Then, the mixture was centrifuged to collect the nanoparticles and afterwards it was dried in an oven at 60°C for 12 h.

2.4. Preparation of the $CoFe_2O_4$/GCE: First, the bare GCE was polished with alumina powder on a soft polishing cloth and then rinsed ultrasonically in a solution of 50:50 ethanol and water for 10 min to remove contamination from the electrode surface. The pre-treatment of the electrode, cyclic scanning was carried out in the potential range of −0.5 to 1.2 V at a scan rate of 100 mV s^{-1} in 0.1 M sulphuric acid (20 cycles) until the stable cyclic voltammograms (CVs) were obtained [27]. Finally, it was rinsed with doubly distilled water and dried. The suspension was prepared by adding of 0.0050 g (0.005 g/ml) of $CoFe_2O_4$ synthesised to distilled water. Then, 5 µl of prepared suspension was dropped on the surface of GCE and dried at room temperature.

2.5. Preparation of the $ZnO@CoFe_2O_4$/GCE: Electrode prepared in the previous step was placed in the solution of 0.03 M of Zn(NO_3)$_2$.4H$_2$O and 0.1 M of KNO_3 (supporting electrolyte) and under stirring applied potential of −0.3 V (versus SCE) for 200 s. Hydroxide ions (OH$^-$) are produced during the reduction process of the water (H_2O) with NO_3^- ions and OH$^-$ reacts with Zn^{2+} to form the complex compound. Finally, the electrode prepared was transferred to the oven at 50°C for 3 h to form ZnO.

2.6. Preparation of the ZnO/GCE: The ZnO/GCE sensor was also manufactured in the same method as described in Section 2.5 without modification with $CoFe_2O_4$.

3. Results and discussion

3.1. Chemical reactions of ZnO synthesis: In this synthesis, according to Hambali et al. [30] Zn(NO_3)$_2$ decomposes to Zn^{2+} ions and NO_3^- ions. OH$^-$ ions are produced during the reduction of H_2O with NO_3^-, and in the next step OH$^-$ reacts with Zn^{2+} to form zinc hydroxide [$Zn(OH)_2$]. At high temperature, the formed Zn$(OH)_2$ is changed into ZnO.

3.2. Morphology and structure of the modified electrodes: Scanning electron microscope (SEM) images were used to probe nanoparticle structure and the morphology of the prepared sensor surface. Figs. 1a and b show the SEM images of $CoFe_2O_4$/GCE and $ZnO@CoFe_2O_4$/GCE with different magnifications. Also, according to quantitative EDX analysis of $ZnO@CoFe_2O_4$ which is shown in Fig. 1c, the mole ratio of iron to cobalt is twice which corresponds to the molecular formula of $CoFe_2O_4$.

3.3. Electrochemical behaviour of AC at the surface of bare GCE and modified electrodes: Comparison of electrochemical

behaviours of AC at the surface of GCE, $CoFe_2O_4$/GCE and $ZnO@CoFe_2O_4$/GCE was carried out using cyclic voltammetry (CV) in 0.1 M of phosphate buffer (pH = 7) solution containing 0.5 mM of AC. Fig. 2 shows CVs of the modified electrodes in comparison with CVs of GCE in 1×10^{-4} M of AC. Owing to the electrocatalytic activity, the oxidation peaks shift to the left.

According to Fig. 2, low redox activity oxidation peak for AC was observed at the unmodified electrode. $ZnO@CoFe_2O_4$/GCE shows a sharp oxidation peak at +0.36 V, and also a relatively good reduction peak at potential of +0.3 V was observed. The currents of this electrode compared with ZnO/GCE and $CoFe_2O_4$/GCE have also been improved. Indicating an increase in electron transfer due to the large surface area of the prepared sensor with nanoparticles. In these voltammograms, the anodic and cathodic peaks
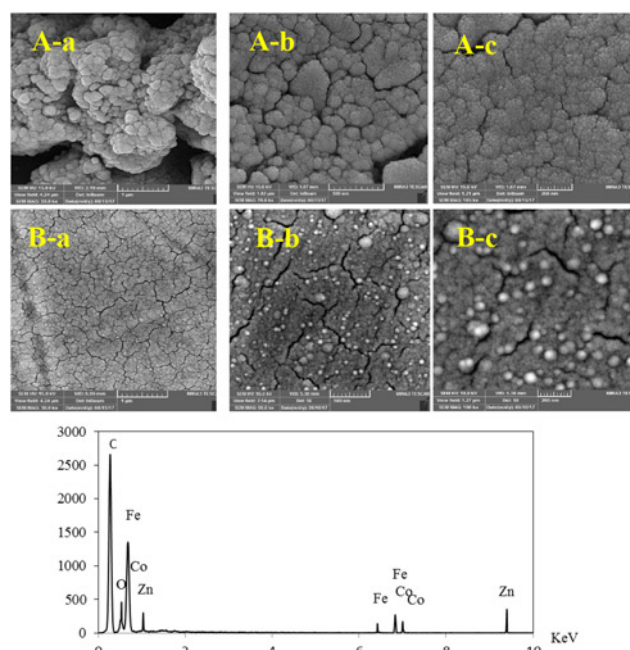
Fig. 1 *SEM images of*
a $CoFe_2O_4$
b $ZnO@CoFe_2O_4$ with different magnifications
c EDX patterns of $ZnO@CoFe_2O_4$
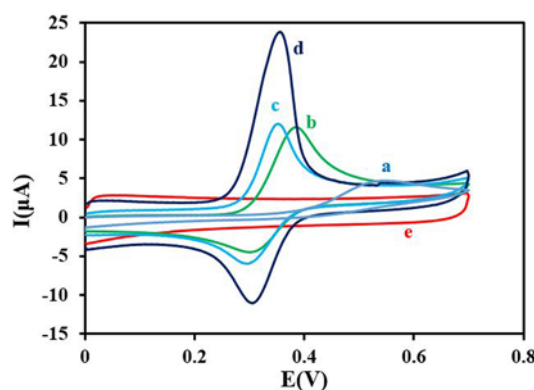
Fig. 2 *CVs of 1×10^{-4} M of AC in 0.1 M of phosphate buffer (pH = 7) at the*
a Bare GCE
b ZnO/CGE
c $CoFe_2O_4$/GCE
d $ZnO@CoFe_2O_4$/GCE
*e* Voltammogram is the CV of $ZnO@CoFe_2O_4$/GCE in the absence of AC, scan rate: 0.05 V s^{-1}

are related to the electrocatalytic oxidation electrochemical reaction of AC, as shown in Fig. 3.

3.4. Effect of pH: The effect of pH values on the AC oxidation peak at the prepared sensor was investigated in 0.1 M of phosphate buffer solution containing 0.0125 μM of AC in the pH range of 2–11, at scan rate of 50 mV s^{-1}. The resulting voltammograms are shown in Fig. 4a. As shown in Fig. 4a, the anodic peak potential due to the participation of proton(s) in the oxidation peak potentials of AC shifted negatively with an increase in pH.

Fig. 4b shows the diagram of relationship between pH and the anodic peak potentials (E_{pa}) in the pH range of 3–8. In this part of the diagram, a linear dependence with the slope of 0.0543 V/pH was observed and it is found that in the oxidation of AC, the number of protons and electrons is equal. This value of the slope indicates that the electrochemical reaction of AC at the modified electrode surface is a function of the Nernst equation.
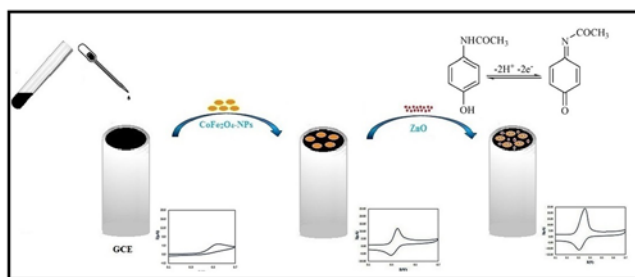
Fig. 3 Schematic illustration of the ZnO@CoFe$_2$O$_4$/GCE sensor fabrication process
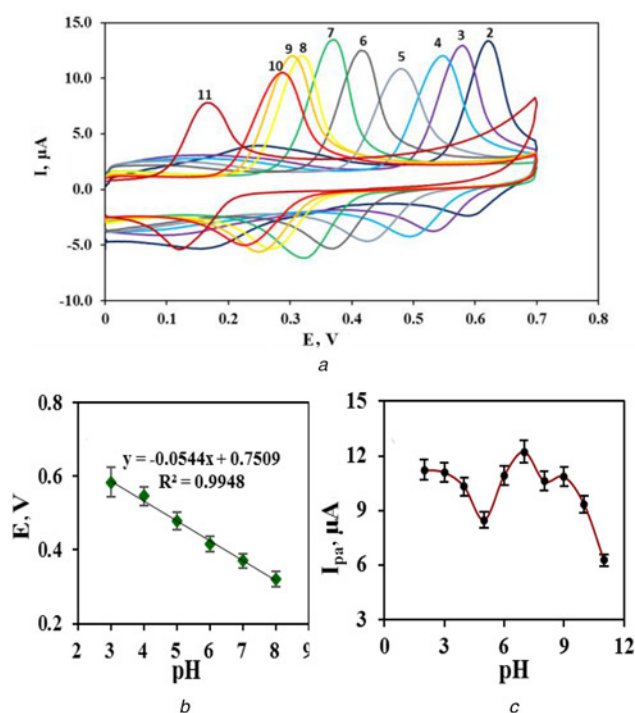
Fig. 4 Resulting voltammograms
a CVs of 1.25×10^{-4} M of AC in 0.1 M of phosphate buffer at different pH values (2–11)
b Linear relationship of E_{pa} versus pH
c Effect of pH on the oxidation peak currents
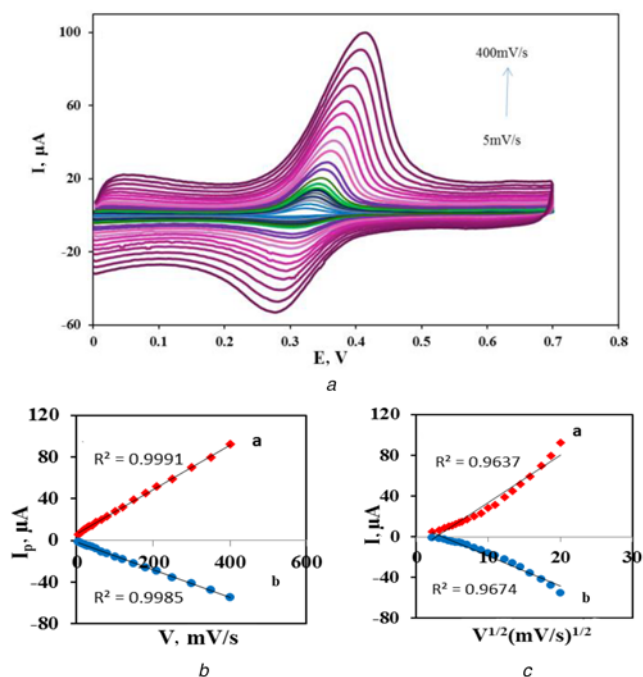
Fig. 5 Effect of scan rate
a CVs of 2.5×10^{-4} M AC in 0.1 M of phosphate buffer (pH = 7) on the ZnO@CoFe$_2$O$_4$/GCE at different scan rates from 5 to 400 mV s^{-1}
b Linear relationship of (a) anodic peak currents (I_{pa}) and (b) cathodic peak current (I_{pc}) of AC versus scan rate
c Relationship of (a) anodic peak currents (I_{pa}) and (b) cathodic peak current (I_{pc}) of AC versus square root of scan rate

On the basis of the diagram of the effect of AC anodic peak currents (I_{pa}) in different pH, also the importance of measuring of pH in biological conditions, the best pH for this research work was obtained pH = 7 (Fig. 4c).

3.5. Effect of scan rate: To investigate the effect of scan rate, the CVs of the prepared sensor in the in 0.1 M of phosphate buffer (pH = 7) containing 2.50×10^{-4} M of AC were recorded at the scan rates from 5 to 400 mV s^{-1} (Fig. 5a).

According to Fig. 5b, there is linear relationships between the anodic peak current (I_{pa}), the cathodic peak current (I_{pc}) and scan rate (V). Moreover, this result shows that the electrochemical process is controlled by the absorption mechanism.

3.6. Calculation of effective surface area of ZnO@CoFe$_2$O$_4$/GCE sensor: To calculate the effective surface of the ZnO@CoFe$_2$O$_4$/GCE, the GCE was first modified in optimal conditions. Then, cyclic voltammetric technique was used at various scan rates in the solution of 0.1 M of KCl (supporting electrolyte) containing 1.0 mM of [K$_4$Fe(CN)$_6$]. It becomes possible to calculate the effective area of electrode surface using the obtained voltammograms (Fig. 6a), the diagram of relationship between K$_4$Fe(CN)$_6$ anodic peak currents (I_{pa}) and the square root of scan rate (Fig. 6b) and according to Randles–Sevcik [$I_{pa} = (2.69 \times 10^5)n^{3/2}ACD^{1/2}v^{1/2}$] [31], where n is the number of exchanged electrons of K$_4$Fe(CN)$_6$, D is diffusion coefficient [for K$_4$Fe(CN)$_6$ is 7.6×10^{-6} cm^2 s^{-1}], C is the concentration of the K$_4$Fe(CN)$_6$ (1×10^{-6} mol/cm^3), V is the scan rate (V s^{-1}) and A expresses the effective surface area of the modified electrode (cm^2). I_{pa} is the anodic peak current (A). The active surface area of the modified electrode was 0.70 cm^2.

Effective surface area of electrode compared with geometric area of electrode (0.0314 cm^2) has been increased more than twice.
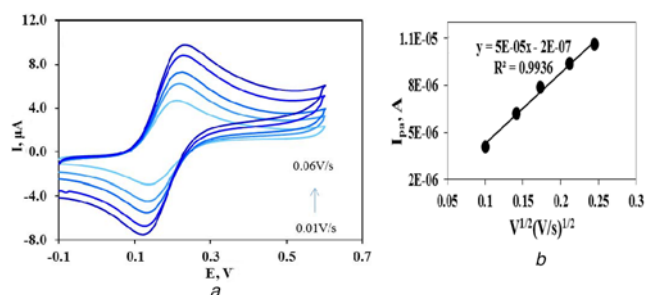
Fig. 6 *Effective area of electrode surface*
a CVs of 0.001 M of $K_4Fe(CN)_6$ in 0.1 M of KCl on the ZnO@CoFe$_2$O$_4$/GCE at different scan rates (10, 20, 30, 45 and 60 mV s^{-1})
b Linear relationship between anodic peak currents (I_{pa}) of $K_4Fe(CN)_6$ and square root of scan rate
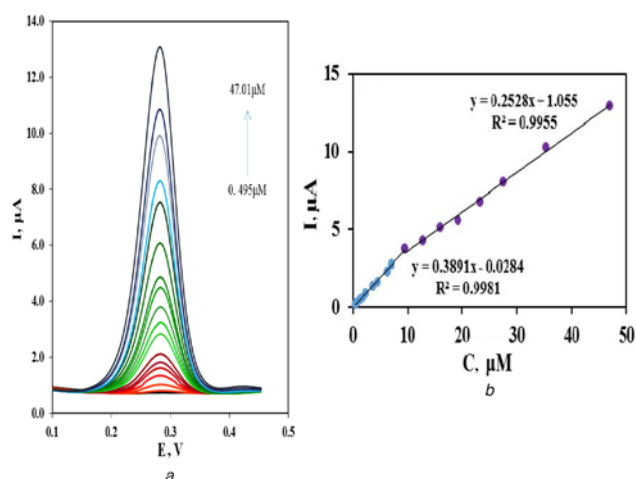
Fig. 7 *Study of DPV behaviour of AC on ZnO@CoFe$_2$O$_4$/GCE sensor*
a DPVs of ZnO@CoFe$_2$O$_4$/GCE for the increasing concentrations of AC in 0.1 M of phosphate-buffered saline (pH = 7). Pulse amplitude: 50 mV and scan rate: 0.05 V s^{-1}
b Calibration plot for the various concentrations of AC

Table 1 Results of recoveries of AC in drug samples[a]

Drug samples	Initial AC	AC added, μM	AC found, μM	RSD, %	Recovery
tablet	4.30	0.0	4.25	1.42	—
	4.30	5.0	9.04	1.30	100.8
oral drop	3.30	0.0	3.32	2.20	—
	3.30	1.50	4.75	1.47	95.33

[a]Number of experiments was three.

Hence, response intensification of modified electrode compared with pure CG electrode (CGE) can be expressed as a result of increment in effective surface of electrode.

3.7. Study of difference pulse-voltammetry (DPV) behaviour of AC on ZnO@CoFe$_2$O$_4$/GCE sensor: Differential pulse voltammograms (DPV) of ZnO@CoFe$_2$O$_4$/GCE sensor for the various concentrations of AC are shown in Fig. 7*a*. These voltammograms have been recorded in optimal conditions. Afterwards, increasing concentrations of AC were added to solution and finally their DPV was recorded. The response of the ZnO@CoFe$_2$O$_4$/GCE was linear over the AC concentration range of 0.495–9.53 and 9.53–47 μM (Fig. 7*b*). On the basis of signal-to-noise ratio of 3, in the first part of the calibration curve, the limit of detection (LOD) was found to be 0.36 μM.

3.8. Analysis of real samples: The practical application of the prepared sensor was tested by determining the concentrations of AC in some drug samples such as oral drops and tablets. In the determination of AC in the sample of oral drops, according to the calculations and information written on the drug package, concentration of AC in the electrochemical cell was estimated as 3.3 μM. Also this value in the tablet sample in the electrochemical cell was estimated as 4.3 μM. Afterwards, concentrations of AC in these samples were measured by differential pulse voltammetric using standard addition method and the same values were obtained with the least error. These measurements were repeated three times. The relative standard deviations for oral drop and tablet were obtained 2.2 and 1.4%. To check the accuracy and recovery efficiency of the proposed method, AC spiked was used and Table 1 was obtained.

Performance of the proposed method is compared with the previously reported methods and the results are demonstrated in Table 2.

4. Conclusion: CoFe$_2$O$_4$ magnetic nanoparticles were chemically synthesised and coated on the electrode surface and ZnO nanoparticles were electrochemically synthesised on the resulting electrode surface. Electrochemical synthesis of ZnO on the electrode surface was optimised and important parameters such as effect of pH, scan rate, repeatability and electrode stability were studied and effective surface of modified electrode was increased compared with pure GCE and its response was improved for AC. The resulting electrode has suitable sensitivity, stability and good repeatability for AC, and hence it can be used for measuring AC in real samples. Using DPV technique and ZnO@CoFe$_2$O$_4$/GCE, it is possible to get low detection limit for AC.

Table 2 Comparison of the performance of the proposed method with previously reported methods

Electrode modifier	Measurement method	Linear range, μm	LOD, μm	References
GCE – Nafion, ruthenium (IV) oxide	Square wave voltammetry	5–250	1.2	[9]
GCE – Cu/TTCA	CV	20–5000	5	[10]
GCE – CNT	squarewave voltammetry	1–2000	0.25	[11]
GCE – C/Ni	differential pulse voltammetry	7.8–110	—	[12]
GCE – TiO$_2$, PAY	differential pulse voltammetry	12–120	2	[5]
carbon paste – CoFe$_2$O$_4$	CV	0.1–200	0.036	[7]
carbon paste – graphene, CoFe$_2$O$_4$	squarewave voltammetry	0.03–12	0.025	[6]
GCE – Ni–Al–hydrochlorofluorocarbon	hydrodynamic amperometry	3–1500	0.8	[2]
GCE – FeS, rGO	differential pulse voltammetry	5–300	0.18	[1]
GCE – ZnO/CF nanocomposite	differential pulse voltammetry	0.495–9.53 9.53–47.00	0.36	this work

6   References

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