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Synthesis, characterization, and electrocatalytic ability of γ -Fe₂O₃ nanoparticles for sensing acetaminophen

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Maghemite (γ -Fe₂O₃) nanoparticles have been synthesized using co-precipitation method followed by chemically induced transition process. As prepared nanoparticles have been analyzed by X-ray diffraction, Raman and FTIR spectroscopies which reveal the γ -Fe₂O₃ phase. These γ -Fe₂O₃ nanoparticles have been used to modify the glassy carbon electrode (GCE) to form nano γ -Fe₂O₃ modified GC electrode for electrochemical sensing of acetaminophen (C₆H₉NO₂) using potential controlled cyclic voltammetric (CV) technique. The obtained modified electrode shows an excellent electrocatalytic ability to sense acetaminophen in 0.1 M KCl supporting electrolyte. In addition, a significant enhancement in anodic peak current has been observed using nano γ -Fe₂O₃ modified GC electrode than the bare electrode. The CV plots reveal that redox peaks have been linearly co-related to the acetaminophen concentration in the range of 0.031 mM to 1 mM with sensitivity \sim 30.78 μ A/mM.

Keywords: γ -Fe₂O₃, Modified GC electrode, Electrochemical sensing, CV, Acetaminophen

1 Introduction

Magnetic nanoparticles are important class of synthetic nanostructure materials, because they exhibit exciting physical and chemical properties which can be exploited in various physical to biomedical applications. Iron oxides and their nanoparticles are ubiquitous in the environment and have been investigated due to their properties and functions in both natural and engineered systems¹. The polymorphic nature of iron oxides is well-known, and the polymorphs which are most frequently found in the nature are magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and hematite² (α -Fe₂O₃). Among them, the maghemite (γ -Fe₂O₃) is a technologically important compound, which is extensively used for the production of magnetic materials and catalysts and gained much attention as a result of their fundamental and technological importance³. Various synthesis methods such as chemical precipitation^{4,6}, chemically induced transition⁷, thermal decomposition^{8,9}, hydrothermal synthesis¹⁰, and sol-gel technique¹¹ etc. have been used to synthesize γ -Fe₂O₃ nanoparticles. Among these methods, the coprecipitation is the most common to prepare synthetic iron oxide nanoparticles,

where the chemical reactions results in to the synthesis directly or via precursor by subsequent heat process¹². Iron based hydroxide (Ferric hydroxide) is chemically stable but magnesium hydroxide easily decomposes when it is heated in aqueous solution⁷. In the present work, a composite precursor consisting of a mixture of FeOOH and Mg(OH)₂ was used in co-precipitation method, and the γ -Fe₂O₃ nanoparticles were subsequently prepared by thermally treating the precursor in FeCl₂.4H₂O solution. The sensing capability of nanostructured iron oxides for different gases and biosensors is of great interest for many researchers. Recently, maghemite (γ -Fe₂O₃) nanostructures have been used as an electroactive material for electrochemical sensing of different compounds¹³⁻¹⁷. Acetaminophen (Paractamol or Tylenol) (C₈H₉NO₂) is widely used antipyretic and analgesic drug¹⁸. It is an appealingly alternative drug for those who are sensitive to aspirin. It reduces, control and cure fever, headache, and mild-moderate pain associated with headache, backache, arthritis and postoperative pain in different organs of human beings¹⁹. In general, the controlled dose of acetaminophen does not exhibit any harmful side effect, but the overdose or any hypersensitivity of acetaminophen can results in the accumulation of

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toxic metabolites, which may cause severe and fatal hepatotoxicity and nephrotoxicity side effects²⁰⁻²². Therefore, an efficient, sensitive, simple, and accurate analytical techniques for the determination of acetaminophen is required. Electrochemical methods are preferred to determine acetaminophen in the pharmaceutical and medical applications due to their fast, cost effective, and accuracy in the detection. Acetaminophen consists of benzene ring core substituted by a electrochemical active phenolic hydroxyl group, which oxidize electrochemically. Literature survey revealed that the various methods and materials were used to modify the electrodes in electrochemical sensing of acetaminophen²³⁻²⁶. However, to the best of our knowledge, the electrochemical sensing of acetaminophen using of maghemite (γ -Fe₂O₃) nanoparticles has not been reported. In the present study, we have synthesized iron oxide with maghemite (γ -Fe₂O₃) phase nanoparticles and used them to modify the glassy carbon (GC) electrode in order to sense the acetaminophen by potential controlled cyclic voltammetric (CV) electrochemical technique.

2 Experimental Details

2.1 Synthesis γ -Fe₂O₃ nanoparticles

The nanoparticles of γ -Fe₂O₃ were synthesized using co-precipitation method followed by chemical-induced transition process. Firstly, the precursor was synthesized by using the co-precipitation method. Finally, the nanoparticles were prepared by thermally treating the precursor in FeCl₂.4H₂O solution through chemical-induced transition process. All the chemicals in the experiment were of analytical grade and used without further purification. The aqueous solutions of FeCl₃.6H₂O (20 mL, 1 M) as an iron source, Mg(NO₃)₂.6H₂O (5 mL, 2M; with the addition of 4 drops of 37% HCl), NaOH (250 mL, 0.7 M), and FeCl₂.4H₂O (200 mL, 0.25 M) were prepared using de-ionized water. Aqueous solution of FeCl₃.6H₂O and Mg(NO₃)₂.6H₂O were added successively to aqueous solution of NaOH. The resulting solution was vigorously stirred and heated upto boiling for 10 min. The brownish color precursor consisting of a mixture⁷ of FeOOH and Mg(OH)₂ gradually precipitated as the heating stopped. Finally, the precursor was added to FeCl₂.4H₂O solution, which was heated to boiling point for 30 min with vigorous stirring. The nanoparticles were precipitated gradually after the heating was stopped. The produced precipitates were collected by centrifugation, filtered and

washed several times with de-ionized water and then dried at 65 °C for 2 h in an oven. The resultant product of γ -Fe₂O₃ nanoparticles were used for further characterization and to modify the glassy carbon electrode (GCE) for electrochemical sensing of acetaminophen.

2.2 Characterization techniques

The phase, crystal structure and particle size of the sample were examined by X-ray diffraction (XRD) using a Siemens diffractometer D5000 with CuK α radiation (1.5406 Å). A Renishaw Raman microspectrometer RM2000 equipped with CCD camera, Leica microscope and 10X magnification objective was used for Raman spectroscopy. Cyclic voltammetric (CV) measurements were performed on BASI cell stand electrochemical workstation with a conventional three-electrode cell configuration using KCl (0.1 M) as supporting electrolyte. Acetaminophen (98% pure) was purchased from Acros organics. A 5 \times 10⁻³ M stock aqueous solution of acetaminophen was made for electrochemical sensing. γ -Fe₂O₃ nanoparticles modified glassy carbon (GC) having diameter 1.6 mm was used as working electrode for sensing acetaminophen. Ag/AgCl (+0.222 V vs NHS at 25 °C) was used as reference electrode. A platinum wire was used as the counter electrode in three electrode cell. The three electrode arrangement was placed in electrochemical cell containing the test solution, to verify the modification. The system was purged with ultrapure nitrogen gas for five minutes to remove the excess oxygen prior to each CV measurements. The measurements were carried out in the potential range from 1000 mV to -1000 mV at 100 mV/s scan rate.

2.3 Preparation of nano γ -Fe₂O₃ modified GC electrode

The bare GC electrode was modified by γ -Fe₂O₃ nanoparticles for electrochemical sensing of acetaminophen. Prior to modification, the GC electrode was cleaned by polishing with nanopowder of aluminum oxide slurry to a mirror surface using pads of different porosity followed by rinsing thoroughly with acetone and de-ionized water several times. For preparing the γ -Fe₂O₃ nanoparticles modified GC electrode, 2 mg powder of γ -Fe₂O₃ nanoparticles was dispersed into 2 mL of de-ionized water under ultrasonic agitation for 30 min. The 4 μ L suspension of γ -Fe₂O₃ nanoparticles were coated on the cleaned surface of GC electrode and dried at room temperature in open air atmosphere for 2 h. The dried modified GC electrode was used for CV measurements.

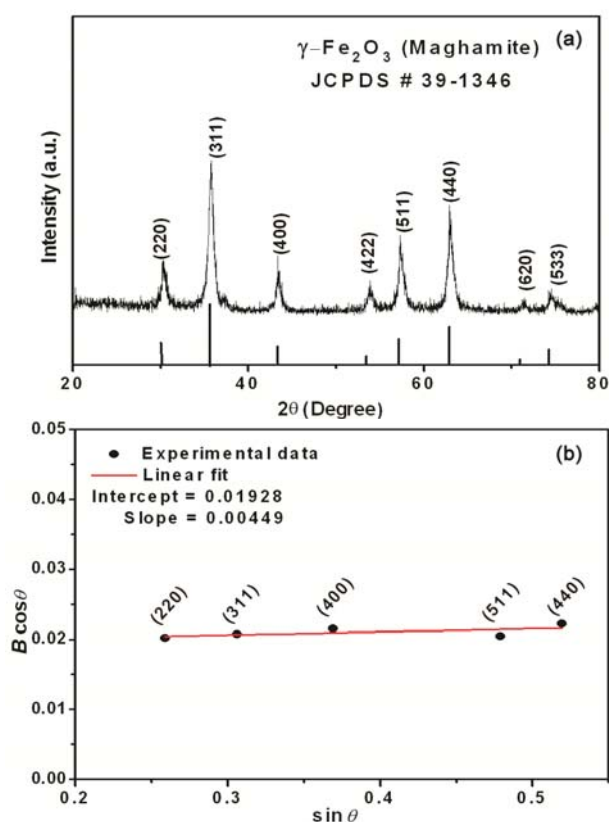


Fig. 1 — (a) XRD patterns and (b) Williamson-Hall plot ($\sin\theta$ versus $B\cos\theta$, fitted to a straight line) for of as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals.

3 Results and Discussion

3.1 XRD studies

The phase of as-prepared nanocrystals of $\gamma\text{-Fe}_2\text{O}_3$ phase was investigated by XRD. Figure 1 shows the XRD patterns and Williamson-Hall plot of as-prepared nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$. The sharp peaks in XRD patterns indicate that the as-prepared nanoparticles are well crystallized, whereas the peak broadening clearly indicates the formation of nanocrystals of small size in the sample. Figure 1(a) shows the XRD patterns of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The diffraction peaks at 30.12° , 35.67° , 43.36° , 53.84° , 57.29° , 62.64° , 71.42° and 74.52° are indexed to (220), (311), (400), (422), (511), (440), (620) and (533), respectively. The peak positions and relative intensities match quite well with inverse spinel structure of maghemite according to JCPDS card No. 39-1346, confirming the presence of $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals.

It is well-known that the crystallite size and the internal strain influence the line broadening in the XRD pattern. The crystallite size (D) was obtained by fitting the following Williamson-Hall equation²⁷ using XRD data of as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles:

$$B \cos \theta = \frac{K\lambda}{D} + 2\epsilon \sin \theta \quad \dots (1)$$

where B is the full width half maximum (FWHM) of a particular diffraction peak of XRD due to strain and size effect in radians, θ is the Bragg's angle and K is a constant equal to 0.9, λ is the wavelength used in XRD instrument ($\text{CuK}\alpha$: $\lambda=1.54 \text{ \AA}$), D is the coherent scattering length (crystallite size) and ϵ is the internal strain (in %). The high intense dominating reflection peaks of the XRD patterns were used in the line broadening analysis of the samples. Figure 1(b) shows the Williamson-Hall plot ($\sin\theta$ versus $B \cos\theta$) fitted to a straight line. The crystallite size (D) of as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles calculated is found to be 7.18 nm. The crystallite size (D) was also calculated from Scherrer formula²⁸:

$$D = \frac{K\lambda}{B \cos \theta} \quad \dots (2)$$

The peak broadening at lower angle is more meaningful for the calculation of particle size; therefore the particle size of as-prepared nanoparticles was also calculated using high intensity peak (311) at 2θ value 35.67° for $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The calculated particle size is found to be 6.69 nm.

3.2 Raman and FTIR spectra

Raman spectroscopy is very sensitive in differentiating various phases of iron oxides. It is hard to identify the exact phase of iron oxide by XRD measurements due to very similar lattice characteristics among different structural phases of iron oxides. The reduction of the dimension of matter domains down to the nanometer scale also induces quantum confinement of the electronic and vibrational wave functions. Subsequently, the Raman peak shifts progressively to lower energies²⁹, and the line shape becomes gradually broader and asymmetric as the structure size becomes smaller³⁰. Figure 2(a) shows the typical Raman spectrum of as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals. It exhibits three characteristic Raman active phonon modes of $\gamma\text{-Fe}_2\text{O}_3$ at 361 cm^{-1} (T_{2g}), 504 cm^{-1} (E_g), and 683 cm^{-1} (A_{1g}). It is observed from the Raman spectrum that there is a well consensus on the reported data of various researchers³¹⁻³⁵. Slight shifting towards lower wavenumbers, broader and asymmetric in all modes may be due to small size of $\gamma\text{-Fe}_2\text{O}_3$ crystals, which is common for nanoparticles. Absence of other iron oxide phases was observed in the Raman spectra of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, which is in good agreement with the XRD results.

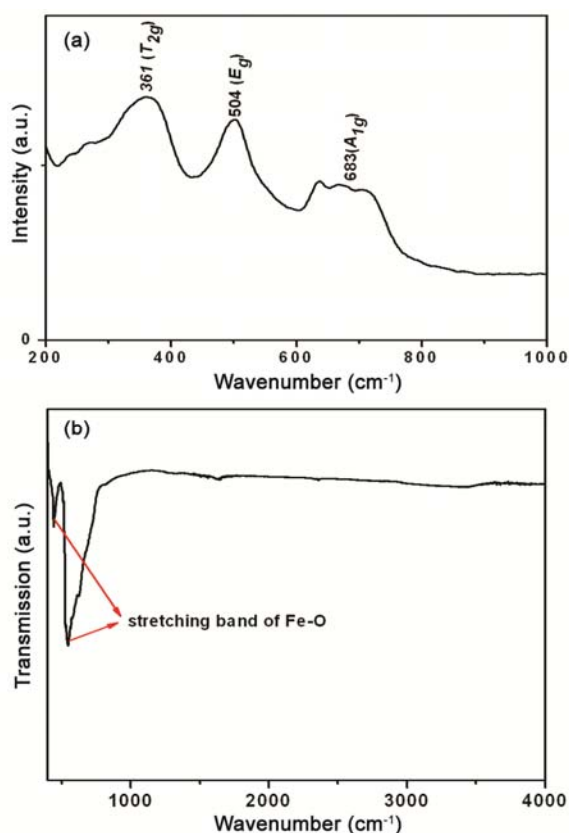


Fig. 2 — (a) Raman spectra and (b) FTIR spectra of as-prepared γ -Fe₂O₃ nanocrystals.

Figure 2(b) shows the FTIR spectra of as-prepared γ -Fe₂O₃ nanoparticles in the spectral range 400-4000 cm^{-1} . The bands in the range 400-750 cm^{-1} are ascribed to the stretching vibration of Fe-O excited from³⁶ the γ -Fe₂O₃. The spectra shows two characteristic bands of Fe-O at 446 and 547 cm^{-1} . The weak absorption at about 1626 cm^{-1} indicates the presence of a very small amount of absorbed water, which generally nanomaterials absorbed from the environment due to their mesoporous structure. The observed vibration bands at low frequencies region suggest the formation of γ -Fe₂O₃.

3.3 Electrochemical sensing of acetaminophen

The electrochemical characteristics of acetaminophen on nano γ -Fe₂O₃ modified GC electrode were explored. The prepared γ -Fe₂O₃ nanoparticles are used to modify the surface of GC electrode for sensing acetaminophen. Figure 3 shows the CV responses of bare and nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl aqueous solution at a scan rate of 100 mVs^{-1} without (blank) and with 1×10^{-3} M acetaminophen solution. Figure 3(a) shows the CV response of bare

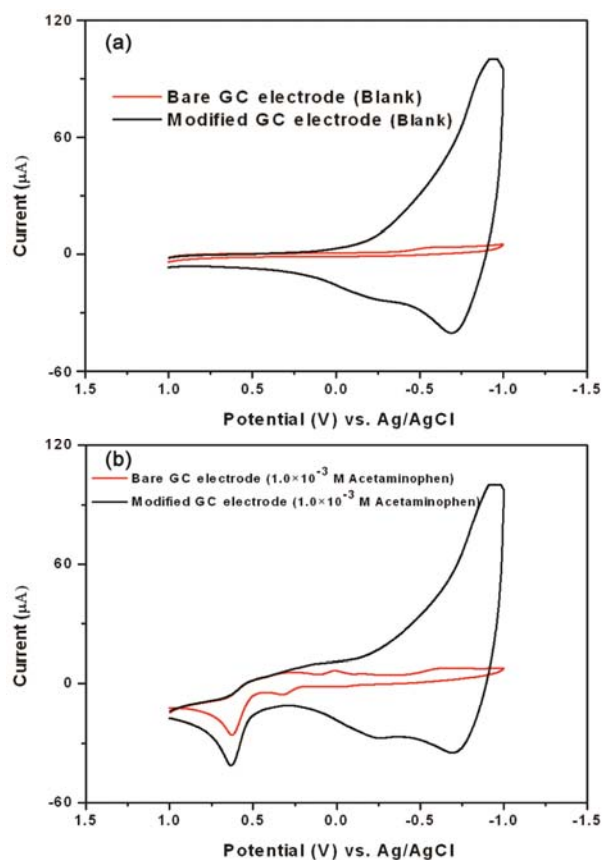


Fig. 3 — CV responses of (a) of bare and nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl solution without (blank) acetaminophen and (b) bare and nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl solution with 1.0×10^{-3} M acetaminophen at scan rate of 100 mVs^{-1} .

and nano γ -Fe₂O₃ modified GC electrode without acetaminophen (blank), which is the evidence for no oxidation response in absence of acetaminophen with both bare and nano γ -Fe₂O₃ modified GC electrode. Figure 3(b) shows CV response of bare and nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl solution with 1.0×10^{-3} M acetaminophen at scan rate of 100 mVs^{-1} . This Voltamogram shows the reduction of acetaminophen. Acetaminophen is a cyclic aromatic amide, which shows a redox process and is oxidized to N-Acetyl-p-benzo-quinone imine (NAPQI) in an aqueous solution³⁷.

The reduction of acetaminophen by bare GC electrode produces two cathodic peaks at 511 mV and 14 mV corresponding to 1.67 μA and 6.59 μA , respectively, along with two anodic peaks at 625 mV and 320 mV corresponding to -25.77 μA and -5.31 μA , respectively. While, the reduction of acetaminophen by nano γ -Fe₂O₃ modified GC

electrode produces a cathodic peak at about 511 mV corresponding to 1.67 μA along with dominating anodic peaks at 630 mV corresponding to -41.31 μA under the same experimental conditions. A large and dominating anodic peak indicates that acetaminophen could yield well-built redox reaction on the nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode, which confirms the electrocatalytic ability of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and successful modification of GC electrode³⁸. The increment in anodic current signal for nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode may be attributed to the increase in the effective electrode surface area due to the coating of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on the surface of GC electrode³⁹. Furthermore, the high current with nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode at about -680 mV indicates that $\gamma\text{-Fe}_2\text{O}_3$ has very strong catalytic action towards the reduction of water to generate hydrogen gas, which can be used for industrial applications in the production of hydrogen.

The dependence of acetaminophen (1.0×10^{-3} M) anodic peak current in 0.1 M KCl solution on scan rate was examined to study the redox reaction process. Figure 4(a) shows the CV responses of

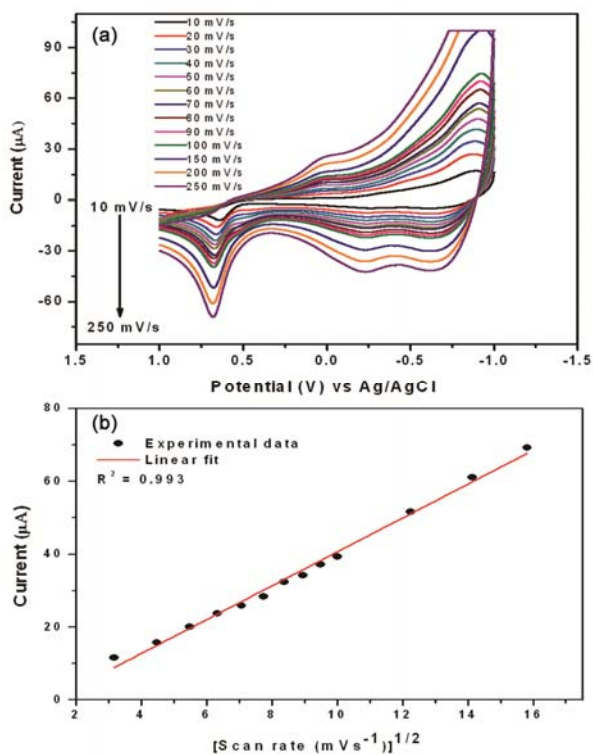


Fig. 4 — CV response of (a) nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode in 0.1 M KCl solution containing 1.0×10^{-3} M acetaminophen at different scan rates and (b) plot of square root of scan rate (v)^{1/2} versus anodic peak current.

acetaminophen on the nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode in 0.1 M KCl solution containing 1.0×10^{-3} M acetaminophen solution at different scan rates. Figure 4(b) shows that the anodic peak current of acetaminophen ($I_{pa}/\mu\text{A}$) was proportional to the square root of scan rate (v/mVs^{-1}) with regression coefficient, $R^2 = 0.993$, suggesting that the electrode process with acetaminophen was controlled by diffusion as expected for a catalytic system. The diffusion coefficient was calculated using the well-known Randal-Sevcik equation at room temperature as given below:

$$i_p = 2.68 \times 10^{-5} n^3/2 AD^{1/2} C v^{1/2} \quad \dots (3)$$

where, i_p is the peak current in ampere, n is the number of electrons transferred in redox process, A is the electrode area in cm^2 , D is the diffusion coefficient in cm^2/s , C is the concentration in mol/cm^3 and, v is the scan rate in V/s . Acetaminophen undergoes the quasireversible reaction with two electrons at GC electrodes¹⁸. The diffusion coefficient calculated by above Equation is found to be 7.51×10^{-4} cm^2/s for nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode at scan rate of 100 mVs^{-1} .

The stability of nano $\gamma\text{-Fe}_2\text{O}_3$ in the sensing of acetaminophen was confirmed by CV responses of nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode in 0.1 M KCl solution containing 1.0×10^{-3} M acetaminophen at scan rate 100 mVs^{-1} for twenty cycles as shown in Fig. 5. It can be seen from this figure that the oxidation potential of acetaminophen remained stable even after

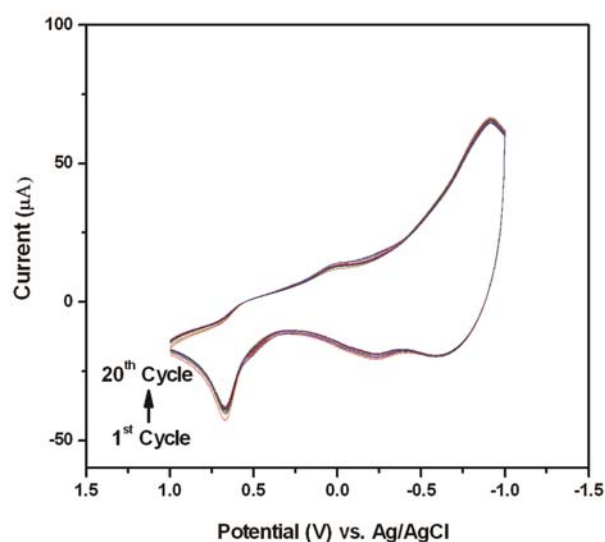


Fig. 5 — CV responses of nano $\gamma\text{-Fe}_2\text{O}_3$ modified GC electrode in 0.1 M KCl solution containing 1.0×10^{-3} M acetaminophen at scan rate of 100 mVs^{-1} for twenty cycles.

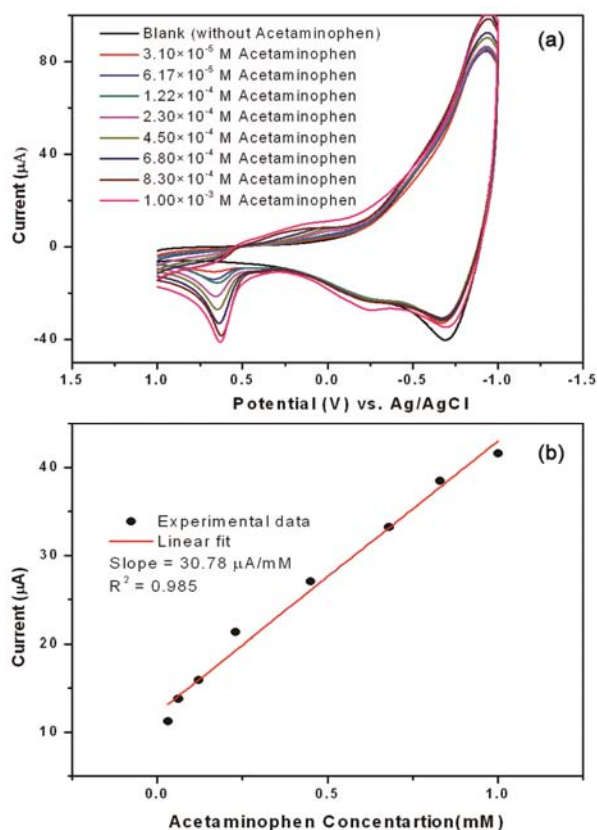


Fig. 6 — CV responses of (a) nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl solution containing different concentration of acetaminophen at scan rate of 100 mVs⁻¹ and (b) Calibration curve between anodic peak current and acetaminophen concentration.

multiple cycles, indicating that the oxidation of acetaminophen is highly stable at nano γ -Fe₂O₃ modified GC electrode.

Figure 6(a) shows the CV plots of nano γ -Fe₂O₃ modified GC electrode in 0.1 M KCl solution containing different concentration of acetaminophen at scan rate of 100 mVs⁻¹. The anodic peak current with nano γ -Fe₂O₃ modified GC electrode is found to be increased with increase in acetaminophen concentration in range 3.1×10⁻⁵ M to 1.0×10⁻³ M. This figure also shows CV response of modified GC electrode without acetaminophen, which did not show any oxidation response in absence of acetaminophen. These results demonstrate the capacity of the nano γ -Fe₂O₃ modified GC electrode for sensing and quantify of acetaminophen. Figure 6(b) shows the calibration plot of nano γ -Fe₂O₃ modified GC electrode as a anodic current response with different acetaminophen concentrations at scan rate 100 mVs⁻¹. The anodic peak current was found to be linearly

co-related with $R^2=0.985$ to acetaminophen concentration in the range 3.1×10⁻⁵ M to 1.0×10⁻³ M. From the linear fit, the current sensitivity was found to be 30.78 μ A/mM for nano γ -Fe₂O₃ modified GC electrode at scan rate of 100 mVs⁻¹.

4 Conclusions

The γ -Fe₂O₃ nanoparticles were successfully synthesized using co-precipitation method. The XRD, and Raman spectroscopy confirms the formation of γ -Fe₂O₃ phase nanoparticles. The electrochemical sensing of acetaminophen by as-prepared nanoparticles was investigated using CV measurements, which proves the electrocatalytic ability of γ -Fe₂O₃ nanoparticles towards acetaminophen. The electrochemical properties of nano γ -Fe₂O₃ modified GC electrode showed a linearity with $R^2=0.985$ in the acetaminophen concentration range of 3.1×10⁻⁵ M to 1.0×10⁻³ M with detection limit 0.075 mM, and sensitivity of 30.78 μ A/mM, respectively. It is concluded that γ -Fe₂O₃ is a good material to prepare solid electrode or to modify the conducting surface of GC electrode for sensing and quantify acetaminophen in terms of non-toxicity, and ease to process. These results suggest the use of γ -Fe₂O₃ as an excellent electrode material in environmental and pharmaceutical fields as an alternative for the analysis of pollutants and/or active ingredients of formulations.

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