Electrochemical sensing of hydrogen peroxide based on nano γ-Fe₂O₃ modified glassy carbon electrode

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Maghemite (γ-Fe$_2$O$_3$) nanoparticles were prepared using chemical synthesis method and used for sensing the hydrogen peroxide. The morphology of the γ-Fe$_2$O$_3$ nanoparticles was characterized by scanning electron microscopy. The γ-Fe$_2$O$_3$ nanoparticles were used to modify glassy carbon electrode (GCE) to form nano γ-Fe$_2$O$_3$ modified GC electrode for electrochemical sensing of hydrogen peroxide (H_2O_2). A potential controlled cyclic voltammetric (CV) technique was performed to sense hydrogen peroxide using nano γ-Fe$_2$O$_3$ modified GC electrode. The nano γ-Fe$_2$O$_3$ modified GC electrode showed excellent electrocatalytic ability towards H_2O_2 in 0.1M KCl supporting electrolyte. A significant enhancement in anodic peak current was observed for the nano γ-Fe$_2$O$_3$ modified GC electrode than those of bare electrode. The electrochemical characteristics of hydrogen peroxide on nano γ-Fe$_2$O$_3$ modified GC electrode had been explored in this research communication.

Keywords: γ-Fe$_2$O$_3$, Modified GC electrode, Electrochemical sensing, CV, Hydrogen peroxide

Introduction

Metal oxide magnetic nanoparticles are of significant interest in today's science and technology due to their wide range of applications in different areas of research such as antimicrobial activities, biosensors, magnetic resonance imaging and drug delivery[1-6]. In particular, iron oxide nanoparticles are known for their fascinating properties as well as potential applications including energy storage and in biomedical field[7-8]. Basically, iron oxide found in 16 different polymorphic phases in nature. Three of them, hematite (α- Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) are widely studied. In comparison to other polymorphs of iron oxide, maghemite (γ-Fe$_2$O$_3$) is of special interest due to its intriguing properties such as its outstanding hysteric properties, thermal stability, non-toxicity and high specific capacitance[9-11]. γ-Fe$_2$O$_3$ possesses cubic spinal structure which arises due to incorporation of Fe^{3+} ions over tetrahedral and octahedral lattice sites formed by oxygen ions. Being magnetic in nature γ-Fe$_2$O$_3$ were able enough for the destruction of the cancer cells by exposing these magnetic nanoparticles to alternating magnetic field and this treatment of cancer is referred as Magnetic hyperthermia.

Several methods have been previously employed by researchers for the phase controlled synthesis of γ-Fe$_2$O$_3$ such as co-precipitation, sol-gel, laser pyrolsis, micro-emulsion, hydrothermal and thermal decomposition[12-18]. Among them co-precipitation method is most popular due to its simplicity, low cost, high yield and better homogeneity. It is efficient method to control the particle size and also there is no need of complex instrumentation for chemical co-precipitation method. This method allows phase controlled growth of γ-Fe$_2$O$_3$ nanoparticles by simply adjusting the concentration of the reactants.

The electrochemical sensing ability of different phases of nanostructured iron oxides in different bio sensors is a recent research interest of many researchers. Currently, maghemite (γ-Fe$_2$O$_3$) nanostructures have been used as an electroactive material for electrochemical sensing of different compounds[19-24]. γ-Fe$_2$O$_3$ nanoparticles are efficient material due to its superior advantages such as it can directly inject into blood vessel because of its convenience to control its particle size as well as it has capability to detect tumor infected cells and healthy tissues separately which makes it suitable candidate for biosensor application. Hydrogen peroxide (H_2O_2) detection scheme have attracted huge interest in biomedical, pharmaceutical and clinical

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research. It is frequently known for oxidizing nature and its excess or deficiency damage lipids and proteins in human body which results in neurodegenerative diseases cancer and Alzheimer[25]. Different techniques such as chemiluminescence, titrimetry, fiber optic device and spectrophotometry have been employed previously for detection of hydrogen peroxide[26-27] Therefore, it is typical task to find appropriate and accurate hydrogen peroxide detection scheme which must be cost and time efficient. Electrochemical sensing is superior technique to detect hydrogen peroxide due to its cost effectiveness, simplicity and accuracy. It is reported earlier that bare solid electrodes due to over potential and slow electron transfer results reduction in electrochemical sensing performance of hydrogen peroxide[28]. Therefore, today's research demands some modification in electrode to overcome the issues of over potential and improve the electron transfer mechanism within the electrode for enhancement in sensing performance.

In this current work, phase controlled synthesis of homogeneous γ-Fe$_2$O$_3$ nanoparticles using chemical co-precipitation method have been reported. Moreover, the electrochemical sensing response of γ-Fe$_2$O$_3$ modified glassy carbon (GC) electrode towards hydrogen peroxide is also investigated. Previously we have also reported facile synthesis of α-Fe$_2$O$_3$ and modified GC electrode with these nanoparticles for electrochemical sensing of acetaminophene[29]. However, electrochemical sensing of γ-Fe$_2$O$_3$ modified GC electrode is subject of interest in today's

technology as they possess efficient sensing response towards hydrogen peroxide.

Experimental Procedures

Maghemite (γ-Fe$_2$O$_3$) nanoparticles were synthesized using chemical co-precipitation method along with chemically induced transition method as discussed in detail in our previous reported research work[30]. Only AR grade (analytical grade) chemicals reagents were used in experiment without any further purification. In the typical phase controlled synthesis process, 1M FeCl$_3$.6H$_2$O aqueous solution along with 2M Mg (NO$_3$)$_2$. 6H$_2$O aqueous solutions were added in 0.7M NaOH solution. The resulting solution was heated at 100°C for 10 minutes under continuous magnetic stirring. As heating stops the precipitate of FeOOH + Mg (OH)$_2$ having brownish color formed which was further added into FeCl$_2$.4H$_2$O solution and stirred for 30 minutes at 100°C giving rise to precipitate of iron oxide nanoparticles. The whole experiment was performed in typical air atmosphere. The resulting precipitate was centrifuged, collected, filtered and washed several times over and over with doubly distilled water. The obtained products are then dried in vacuum oven at 65 $^\circ$C for 2 h. Under this controlled process, the final product γ-Fe$_2$O$_3$ nanoparticles were formed which were used to modify GC electrode for sensing hydrogen peroxide. The schematic diagram of synthesis process of γ-Fe$_2$O$_3$ nanoparticles is shown in Fig. 1.

The morphology of the γ-Fe$_2$O$_3$ nanoparticles were examined from 10,000X order magnification Scanning
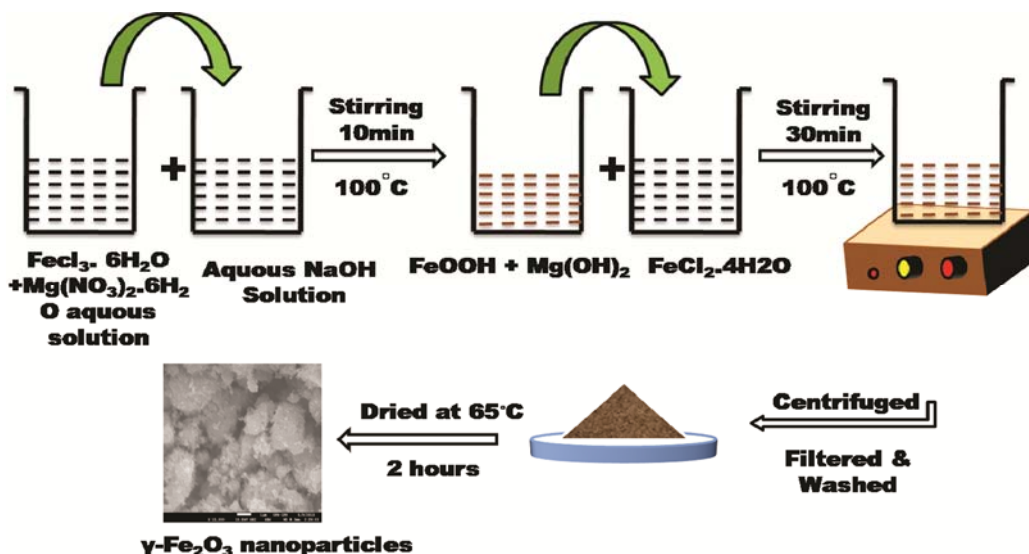

Fig.1 — Schematic diagram of phase controlled synthesis process of γ-Fe$_2$O$_3$ nanoparticles

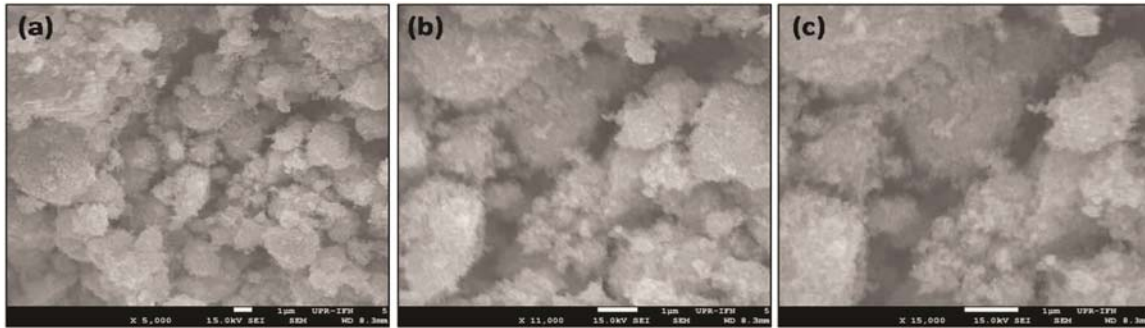Fig. 2 — Scanning electron microscopy (SEM) images of γ-Fe$_2$O$_3$ nanoparticles at different magnifications (a) 5000X (b) 11000X (c) 15000X

Electron Microscope (SEM). UV-Visible spectroscopy gives idea about the band gap of the γ-Fe$_2$O$_3$ nanoparticles. While the magnetic response of the as synthesized γ-Fe$_2$O$_3$ nanoparticles were predicted using Vibrating Sample Magnetometer (VSM) having range 0.00001 to 10000 e.m.u. For electrochemical sensing, Cyclic Voltammetric (CV) response of bare and γ-Fe$_2$O$_3$ nanoparticles modified GC electrode were measured in BASI cell stand electrochemical workstation with a conventional three-electrode system. In typical electrochemical sensing, Ag/AgCl electrode was used as reference electrode. However, γ-Fe$_2$O$_3$ nanoparticles modified GC electrode was used as working electrode and platinum wire was used as the counter electrode for sensing hydrogen peroxide. Nitrogen (ultra pure) gas was used for the removal of O$_2$ present in the system during CV measurements. CV measurements were performed at scan rate of 10 mV/s -100 mV/s.

Results and Discussion

Figure 2 (a-c) shows the Scanning electron microscopic (SEM) microstructures of the as-synthesized γ-Fe$_2$O$_3$ nanoparticles. The SEM images of γ-Fe$_2$O$_3$ nanoparticles for 1µm scale at different magnifications clearly reveal the uniform distribution on the whole and spherical type surface morphology.

Absorption spectra of as-synthesized γ-Fe$_2$O$_3$ nanoparticles were shown in the Fig. 3. The UV-Visible absorption spectra clearly predict that there was no absorption ahead 900 nm.

The Vibrating sample Magnetometer (VSM) was used to analyze the magnetic behavior and hysteresis loop of γ-Fe$_2$O$_3$ nanoparticles in magnetic field range from -20 to 20 KOe. It shows good magnetic behavior having saturation magnetization (M$_s$) 1.05 emu/gm, remanence (M$_r$) 0.0013 emu/gm with slight coercivity (H$_c$) as listed in Table 1. This negligible remanence and coercivity suggest superparamagnetic behavior of γ-Fe$_2$O$_3$ nanoparticles[31]. Magnetic hysteresis loop of γ-Fe$_2$O$_3$ nanoparticles were shown in Fig. 4.
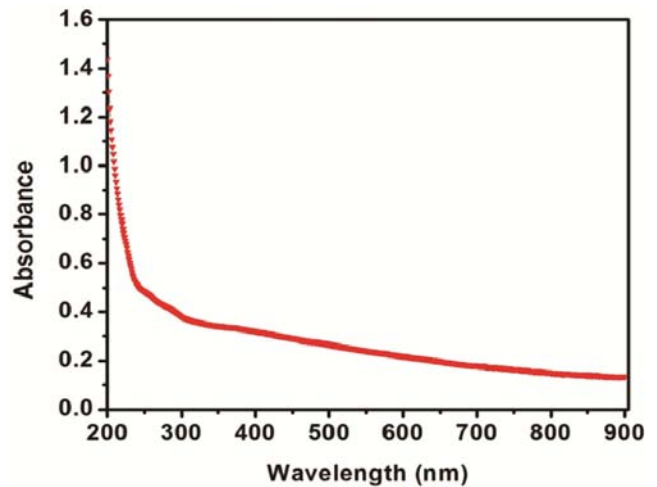

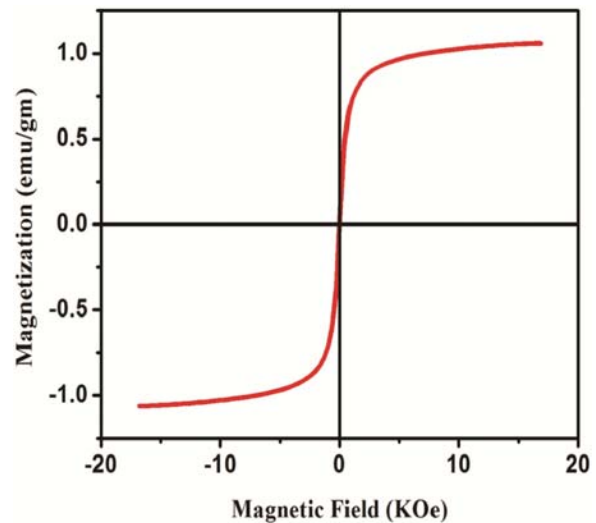Fig. 3 — UV- Visible absorption spectra of γ-Fe$_2$O$_3$ nanoparticles

Fig. 4 — Magnetic hysteresis loop for γ-Fe$_2$O$_3$ nanoparticles

Table 1 — Values for saturation magnetization (M$_s$), remanence (M$_r$), coercivity (H$_c$) and ratio of M$_r$/M$_s$

Sample	M$_s$ (emu/gm)	M$_r$ (emu/gm)	H$_c$ (KOe)	M$_r$/M$_s$
γ-Fe$_2$O$_3$	1.0574	0.0013	0.035	0.0012
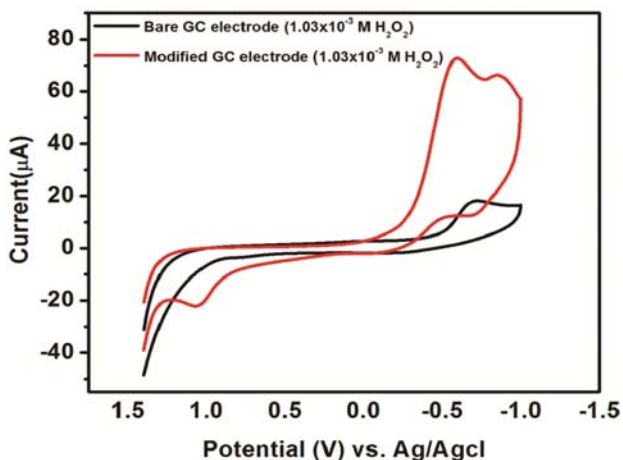
Fig. 5 — CV curves of bare/ γ-Fe$_2$O$_3$ nanoparticles modified GC electrode with 1.03×10^{-3} M   hydrogen peroxide (H$_2$O$_2$) in 0.1M KCl supporting electrolyte at100 mV/s scan rate
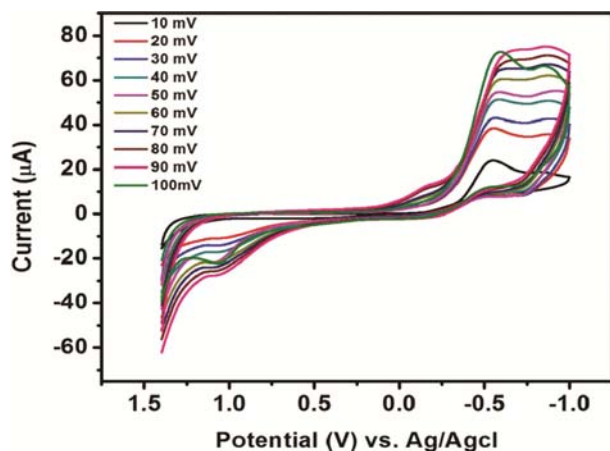

Fig. 6 — CV curves of nano γ-Fe$_2$O$_3$ modified GC electrode with 1.03×10^{-3} M Hydrogen peroxide (H$_2$O$_2$) in 0.1M KCl supporting electrolyte at different scan rates (10-100 mVs^{-1})

Fig. 7 — Plot of square root of scan rate versus anodic peak current of γ-Fe$_2$O$_3$ nanoparticles modified GC electrode with 1.03×10^{-3} M hydrogen peroxide (H$_2$O$_2$) in 0.1M KCl supporting electrolyte

The electrochemical responses of H$_2$O$_2$ on γ-Fe$_2$O$_3$ modified glaasy carbon (GC) electrode were investigated by cyclic voltammetric measurements. Fig. 5 represents the CV curves of bare and γ-Fe$_2$O$_3$ modified GC electrode at scan rate of 100 mV s^{-1} with 1.03×10^{-3} M concentration H$_2$O$_2$ solution in 0.1M KCl supporting electrolyte. It is clear from Fig. 5 that there was no sensing response towards H$_2$O$_2$ on bare GC electrode. While there was sufficient electrochemical response towards H$_2$O$_2$ on γ-Fe$_2$O$_3$ modified glaasy carbon (GC) electrode in the form of large anodic peak potential at 1.0568 V. This large anodic peak potential indicates that H$_2$O$_2$ give rise to redox reaction on γ-Fe$_2$O$_3$ modified GC electrode.

Figure 6 shows the CV curves of nano γ-Fe$_2$O$_3$ modified GC electrode with 1.03×10^{-3} M H$_2$O$_2$ in
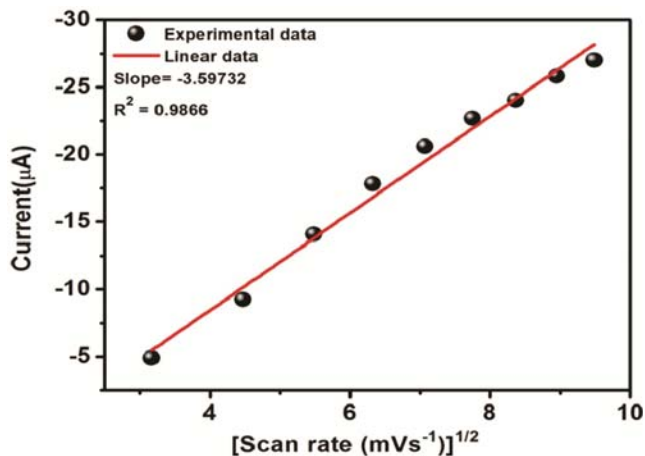
0.1M KCl supporting electrolyte at different scan rates from 10-100 mVs^{-1}. It is clear that anodic peak increases successively with scan rate. The reason for increment in anodic peak for γ-Fe$_2$O$_3$ modified GC electrode may be due to increase in electrode surface area by the modification of GC electrode with γ-Fe$_2$O$_3$ nanoparticles[32].

Figure 7 represents the plot of square root of scan rate versus anodic peak current of γ-Fe$_2$O$_3$ nanoparticles modified GC electrode with 1.03×10^{-3} M concentration H$_2$O$_2$ in 0.1M KCl supporting electrolyte. It indicates that proportionality of anodic peak current over square root of scan rate in range 10-100 mVs^{-1} with $R^2 = 0.9866$, suggesting diffusion controlled nano γ-Fe$_2$O$_3$ modified GC electrode process which is favorable for catalytic system.

Conclusions

Phase controlled synthesis of γ-Fe$_2$O$_3$ nanoparticles were successfully employed by facile chemical co-precipitation method. The Scanning electron microscopy (SEM) images revealed the spherical surface morphology of γ-Fe$_2$O$_3$ nanoparticles. UV-Visible absorption spectra suggest that there is no absorption beyond 900 nm. Magnetic hysteresis loop of γ-Fe$_2$O$_3$ nanoparticles revealed the good magnetic response with saturation magnetization. The electrochemical sensing of hydrogen peroxide by γ-Fe$_2$O$_3$ modified GC electrode was investigated through CV measurements, which suggests its electrocatalytic ability towards H$_2$O$_2$. The square root of scan rate versus anodic peak current graph of γ-Fe$_2$O$_3$ nanoparticles modified GC electrode gives

linearity having $R^2 = 0.9866$ in the 1.03×10^{-3} M concentration H_2O_2 in 0.1M KCl supporting electrolyte The results predicted that as-synthesized γ-Fe_2O_3 nanoparticles are promising candidate for the modification of GC electrode and sensing H_2O_2. It is also concluded that H_2O_2 detection with nano γ-Fe_2O_3 modified GC electrode have potential applications in pharmaceutical and clinical research to cure the neurodegenerative diseases.

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