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Research Article

Electrochemical study of caffeine using iron oxide nanoparticles modified glassy carbon electrode and its electro catalytic activity

Jagadish R^{1,2,4}, Shivaraj Y^{*1}, Chandrasekhar K B³, Mallappa M¹

¹Government Science College, Bangalore, India

²Government First Grade College, Chickballapur, India

³JNTUA-Oil Technological Research Institute, Ananthapuramu, Andhra Pradesh, India

⁴Jawaharal Nehru Technological University, Ananthapuramu, Andhra Pradesh, India

ABSTRACT

Iron oxide nanoparticles were prepared by a simple, convenient and cost effective co-precipitation method using starch. The prepared iron oxide nanoparticles were characterized by XRD, SEM, IR and UV techniques. The size of the nanoparticles was calculated from XRD data using Debye-Scherrer equation. The average particle size was found to be 11 nm. The electrochemical behaviour of caffeine was studied using glassy carbon electrode (GCE) modified with iron oxide nanoparticles by cyclic voltammetry and differential pulse voltammetry using 0.1M acetate buffer solution of pH-7.0. Caffeine gives an oxidation peak at 1.426 V with peak current at -5.6×10^{-5} A for iron oxide NPs modified GCE whereas for unmodified GCE peak potential occurs at 1.426 V with peak current at -5.08×10^{-5} A. The peak current intensity significantly increased while the peak potential shifted to lower oxidation potential, compared with the unmodified electrode. The results clearly indicated that the modified electrode exhibited excellent electro catalytic activity towards oxidation of caffeine.

Keywords: Caffeine; co-precipitation method; Fe₂O₃-GCE; Iron oxide nanoparticles; voltammetry.

INTRODUCTION

Magnetic iron oxide nanoparticles (γ -maghemite) have various applications like magnetic resonance imaging (Williams *et al.*, 2006), magnetic storage media (Sun *et al.*, 2000), drug delivery to targeted organ/cell (Munnier *et al.*, 2008), biosensor applications (Gee *et al.*, 2003) tissue repair and hyperthermia (Gupta *et al.*, 2003). Iron oxide nanoparticles can be synthesized by different methods like co-precipitation method (Venkatesan *et al.*, 2003), sol gel method (Xu *et al.*, 2007), hydrothermal method (Zhang *et al.*, 2008) and thermal decomposition method (Maity *et al.*, 2009) etc. Magnetic iron oxide nanoparticles have been exploited as a potential material for biosensing due to their excellent characteristic like biocompatibility, strong super paramagnetic property and low toxicity (Kim *et al.*, 2001)

Caffeine is a naturally occurring alkaloid which belongs to the class of compounds called xanthenes. It is found naturally in various foods such as coffee, tea, cocoa, chocolates, cola nuts etc. For humans caffeine has

many physiological effects like stimulation of central nervous system, diuresis and gastric acid secretion (Rostagno *et al.*, 2011). However high amount of caffeine is harmful which causes trembling, nausea, nervousness and seizures (Okonny *et al.*, 2005). Hence detection and quantification of caffeine in an important aspect in clinical chemistry. Electrochemical methods have been widely used for the detection of caffeine because of their simplicity, low cost instrumentation, high sensitivity and high selectivity.

In this work iron oxide nanoparticles were synthesized by co-precipitation method using starch which controls the particle size. Iron oxide nanoparticles modified glassy carbon electrode was used for the electrochemical detection of caffeine to improve the sensitivity and selectivity.

EXPERIMENTAL

Materials

Caffeine was purchased from Sigma -Aldrich. Ferrous sulphate heptahydrate, ferric chloride hexahydrate, Starch and other reagents were purchased from Merck. All reagents were of analytical grade. The supporting electrolyte used for all the experiments was 0.1 M acetate buffer solution of pH 7, which was prepared by using 0.1M sodium acetate and pH was adjusted by using acetic acid and sodium hydroxide. All the reagents were prepared using doubly distilled water.

* Corresponding Author

Email: shivaraj_y@rediffmail.com

Contact: +91-9972001267

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Synthesis of Iron oxide nanoparticles

The Iron oxide nanoparticles was synthesized by simple co-precipitation method using biopolymer starch. 100ml mixture of 2:1 molar ratio of ferric chloride hexahydrate and ferrous sulphate heptahydrate was added drop wise under magnetic stirring at 60°C to 1% starch solution taken in a beaker. The pH of the reaction mixture was maintained at 9-10 by adding 0.1M NaOH solution. The precipitate obtained was filtered and washed with 1:1 mixture of water and ethanol. The brownish black precipitate was dried in hot air oven at 50 °C for about 2 hours and finally the solid powder was calcined in a muffle furnace at 400 °C. A brown powder of magnetic iron oxide nanoparticles obtained was characterized by various techniques.

Material Characterization

Powder XRD data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu K α radiation ($k = 1.541 \text{ \AA}$) in the range of 10°–80° with 2°/min scanning rate. The morphology of the Iron oxide nanoparticles was examined by JEOL-JSM-6490 LV scanning electron microscope (Kevex Sigma TM Quasar, USA). Fourier Transform infrared (FTIR) spectra of the product dispersed in a KBr pellet were recorded at room temperature on Agilent FTIR spectrometer (Australia) over the range 400-4000 cm^{-1} . In addition, the optical property of prepared Iron oxide nanoparticles was analyzed via UV-visible absorption spectrophotometer (UV-Vis, Shmidzu).

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) measurements were performed using a CH instruments electrochemical analyzer connected with a three-electrode cell (USA). The Glassy carbon electrode (GCE) and Iron oxide nanoparticles modified Glassy carbon electrode (Fe₂O₃-GCE) was used as a working electrode. A platinum electrode with a large surface area was employed as the counter electrode while the reference was a saturated calomel electrode. CVs was recorded between 0.6 and 1.6 V/SCE at a scan rate of 50 mVs⁻¹.

RESULTS AND DISCUSSION

Crystal Structure and morphological analysis

The phase purity of the Iron oxide nanoparticles was confirmed by X-ray diffraction studies. **Figure.1** shows the XRD pattern of starch assisted Iron oxide nanoparticles prepared in solution phase and the diffraction patterns correspond to the cubic phase of Iron oxide nanoparticles (JCPDF Card No. 39-1346). The diffraction peaks for Iron oxide nanoparticles were observed at $2\theta = 30.54, 36.00, 43.54, 53.82, 57.66$ and 63.28 which can be indexed to (220), (311), (400), (422), (511) and (440) planes of iron oxide NPs respectively. There are no other characteristic impurities peaks were present which also confirm that the Iron oxide nanoparticles obtained is in pure phase. The definite line broadening of the peaks also indicate that the particle

is in the nano meter range. The average crystallite size estimated from the Debye-Scherrer equation (Mote *et al.*, 2012) was found to be 11 nm.

Scanning electron microscope spectroscopy

Scanning electron microscopy is an effective tool to study the surface morphology of nanoparticles. **Figure.2** represents the crystalline structure of Iron oxide nanoparticles, the diameters of the particles grow larger with uneven size distribution and irregular shape. The SEM picture indicates that the Iron oxide nanoparticles are present in starch matrix.

IR spectra of Iron oxide nanoparticles

The structure and chemical compositions of starch assisted Iron oxide nanoparticles were examined in the 400–4000 cm^{-1} regions by using FT-IR spectroscopy analysis as shown in **Figure.3**. A relatively broad band observed at 3328 cm^{-1} , indicating the presence of starch association of the free hydroxyl groups and bonded -OH stretching vibration. The weak absorption bands at 2,941 and 2,828 cm^{-1} were attributed to anti-symmetric CH₂ stretching and C-H stretching vibration of CH₂ groups which correspond to the carbon chain of the biopolymer associated with the Iron oxide nanoparticles (peaks not shown in fig). The absorption band occurring at 1644 cm^{-1} is due to asymmetric C-O stretching vibration. The band at 1095 cm^{-1} is assigned to C-O stretching vibration. The band at 528 cm^{-1} can be assigned to the vibration of Fe-O bond (Jegan *et al.*, 2011). The above results confirm the presence of starch which acts as capping agent and also increases the stability of the nanoparticles.

Optical properties of Iron oxide nanoparticles

The optical absorption spectra of the Iron oxide nanoparticles dispersed in 1:1 water/ethanol were recorded at room temperature in the range 200 nm to 800nm as shown in **Figure.4**. The characteristic absorption maxima of Iron oxide nanoparticles were observed at 383 nm. The absorption of Iron oxide nanoparticles shift towards lower wavelength (blue shift) region as compared with that of bulk iron oxide.

Voltammetry response of Iron oxide NPs modified GCE toward caffeine oxidation

CAF is an electrochemically active species that produce analytically useful voltammetric signals at different working electrodes. Redox process of CAF at Iron oxide nanoparticles modified GCE and non-modified GCE electrode in acetate buffer of pH-7.02 involves irreversible oxidation of CAF manifested as an anodic signal as shown in **figure.5 (A) and (B)**. The anodic signal of CAF at GCE is observed at 1.426 V whereas for Iron oxide nanoparticles modified GCE anodic signal was observed at 1.39 V. The electrochemical oxidation of CAF at the Iron oxide nanoparticles modified GCE shows an excellent electro catalytic activity as compared with non-modified GCE electrode. This is due to

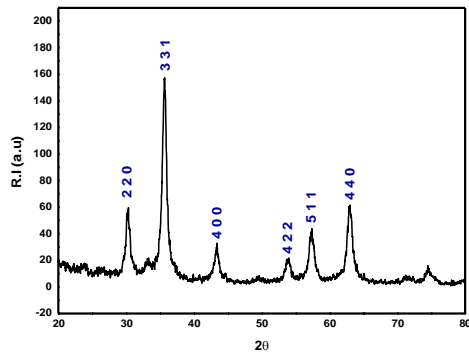


Figure 1: XRD pattern of Iron oxide nanoparticles

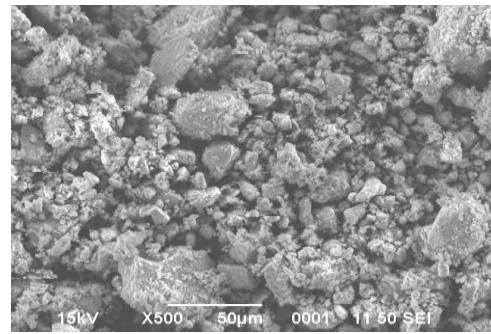


Figure 2: SEM image of the Iron oxide Nanoparticles

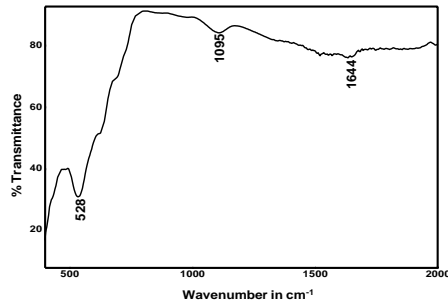


Figure 3: IR Spectra of starch assisted Iron oxide nanoparticles

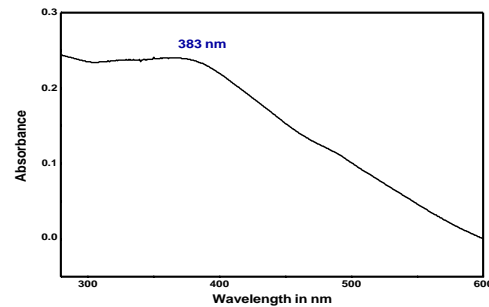


Figure 4: UV-Visible Spectra of Iron oxide nanoparticles

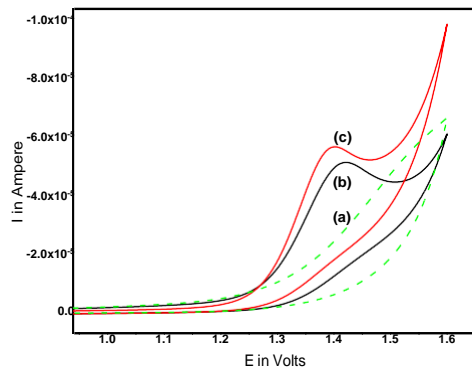


Figure 5(a): (A) CVs

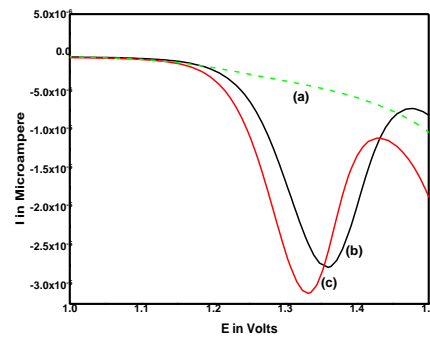


Figure 5(b): (B) DPVs

Figure 5: (A) CVs and (B) DPVs of 0.1mM of CAF on (a) blank, (b) bare GCE and (c) iron oxide modified GCE for pH-7.0 at 50mV/sec

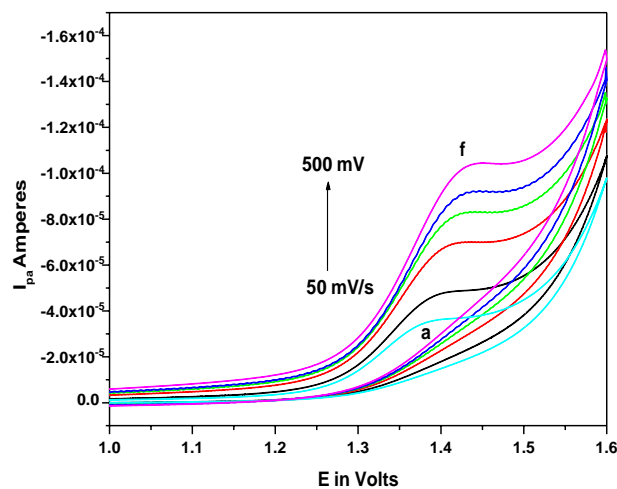


Figure 6: (A) CVs of 100 µM of CAF in 0.1M acetate (pH 7.0) at Fe₂O₃-GCE electrode at different scan rates (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 V/s)

the adsorption/desorption (reorientation) process at electrically charged surface of the electrode. This indicates that the Iron oxide nanoparticles modified GCE exhibited tremendous electro catalytic effect towards oxidation of CAF. The peak current intensity significantly enhanced as well as the peak potential shifted to negative potential, compared with the unmodified electrode. The anodic response of CAF is significantly enhanced in comparison with the non-modified GCE, suggesting that the irreversibility of CAF is significantly improved by using Iron oxide nanoparticles.

Influence of scan rate

Figure 6. Shows the CVs of 100 μM CAF on Fe_2O_3 -GCE in 0.1 M acetate buffer of pH 7.02 at various scan rates. On increasing the scan rate from 0.05 to 0.5 Vs^{-1} , the anodic peak current of CAF increased linearly and the peak potential shifted to small positive values. These results also confirmed that the oxidation of CAF was irreversible. The plots of $\log I_{pa}$ vs. $\log v$ in the scan rate range of 0.05 to 0.4 Vs^{-1} yielded a straight line (Graph not shown) the linear regression equation $\log I_{pa} (\mu\text{A}) = -3.305 + 0.47 \log v (\text{Vs}^{-1})$: ($R = 0.9981$) and with slope of 0.47. This slope value is very close to the theoretical value of 0.5, which is expected for an ideal reaction condition for diffusion controlled electrode process (Pruneanu et al., 2011). In the potential range from 0.05 to 0.4 Vs^{-1} the anodic peak currents were linearly proportional to the scan rate and it can be deduced that the electrochemical oxidation of caffeine at Iron oxide nanoparticles modified GCE is a diffusion-controlled process.

CONCLUSION

Iron oxide nanoparticles were synthesized by a simple coprecipitation method in aqueous media using biopolymer starch. The Iron oxide nanoparticles were used to modify the surface of a glassy carbon electrode for the electrochemical detection of caffeine (CAF) and the performance of GCE was significantly improved due to the excellent electrical conductivity and large surface area of Iron oxide nanoparticles. The modified electrode exhibited a high electro catalytic activity and good selectivity towards the oxidation of CAF which is reflected by a significant increase of the peak current and a shifting of the peak potential towards lower oxidation potential compared with the unmodified GCE.

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