Gadolinium ferrite nano-particle based electrochemical sensor
for detection of acetylsalicylic acid

Yogendra Kumar, Deeksha Gupta, Prabal Pratap Singh*, Dipak Kumar Das*

Department of chemistry, Institute of Applied sciences and Humanities, GLA University, 17 km stone
NH19 Delhi-Mathura Highway, Mathura, India, 281406
*Corresponding authors: prabal.singh@glau.ac.in, deepak.das@glau.ac.in

Abstract
A novel electrochemical sensor based on gadolinium ferrite nano-particle (GdFeO$_3$/GP) has been fabricated for the
detection of aspirin. FESEM and TEM results reveal that synthesized nano materials are in nano range with particle
size of 40 to 45 nm. Cyclic voltammogram of 1µM ASA indicated a single irreversible oxidation peak at 1.1 V
which was 2 fold higher than bare GP electrode. Maximum current value was obtained with supporting electrolyte at
pH-6.0. Hence phosphate buffer solution of pH 6.0 was employed in all experimental work, maintaining scan rate at
100mVs$^{-1}$.

Keywords: Gadolinium ferrite, nano-particle, electrochemical sensors, acetylsalicylic acid, cyclic
voltammetry.

Introduction
Clinically effective pharmaceutical compounds possess biomedical interest. Another name of
acetylsalicylic acid (ASA) is aspirin and is a well known drug for the treatment of inflammation, fever and
headache. Acetylsalicylic acid is in the new variety of water pollutants, having ill impact on potable water
quality and public well being [1]. It is effective in Alzheimer’s disease [2, 3], as well as in the prevention
of cardiovascular disease [4, 5], and in cancer [6]. These kinds of pharmaceutically potential materials
also possess much physiological disorder such as gastric acid secretion and dieresis [7], which are
essential to be analyzed. Previously a number of analytic approaches, like spectrophotometry [8, 9], spectrofluorimetry [10], HPLC [11, 12], Raman spectroscopy [13, 14], and gas chromatography [15, 16] are published reported for determination of acetylsalicylic acid. Unfortunately majority methods are time taking, involve high expense, operational difficulties and poor performance. In contrast, electrochemical methods have advantages of shorter reaction time, lucidity and high reactivity. Recently developed electrodes for efficient determination of ASA are carbon paste electrode [17-23], the mildly oxidized boron-doped diamond electrode [24], the mwCNT-alumina-coated silica nanocomposite modified glassy carbon electrode [25], and sensitive edge plane pyrolytic GP electrode modified with graphene [26].

Here in, we report gadolinium ferrite nano-particle based electrochemical sensor for detection of acetylsalicylic acid. For this, we adopted a simple strategy to synthesize gadolinium ortho-ferite \((\text{GdFeO}_3)\) nano particles. FESEM and TEM results supported the nano range size of the newly synthesized nano materials. The working electrode was prepared by mixing \(\text{GdFeO}_3\) and graphite powder. Finally this electrode was used as electrochemical sensor for the detection of ASA by CV using a phosphate buffer solution of pH 6. The reproducibility and stability of this sensor are also reported in this manuscript.

2. Method & materials

2.1. Reagents and Chemical required

\(\text{Gd}_2\text{O}_3\), \(\text{Fe(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O}\), \(\text{HNO}_3\), paraffin oil and \(\text{HOCH}_2\text{CH}_2\text{NH}_2\) were supplied by Merck (India ) and graphite flakes and aspirin \((\text{C}_9\text{H}_8\text{O}_4)\) were received from Sigma Aldrich, USA. reagents analytical grade reagents were used without further purification. DD water was employed to prepare all solutions.

2.2. Procedure for synthesis of lanthanide orthoferrites np

A solution of \(\text{Gd}_2\text{O}_3\) (1.0 mM) in 50 ml of DD water by made by adding \(\text{HNO}_3\) (3.5 mM) and then heated, until a brownish solution was received. Then \(\text{Fe(NO}_3\text{)}_3\) (1.0 mM), 2-aminoethanol (1.7 mM) and table
sugar (2.5 mM) were mixed in above solution and kept on hot plate at 150°C until evaporated to dryness.
Produced black then got calcined in muffle furnace at 800°C for six hours to yield above targeted nanoparticles.

2.3. Construction of electrode

For electrode preparation, the graphite powder & nano-particles (np) of lanthanides ferrites got grinded (4:1 ratio) uniformly in a mortar and pastel with little paraffin oil to prepare paste, A capillary glass tube (2 mm inner diameter) was filled with the paste, packed tightly by using a metal rod. For electrical contact a platinum wire was inserted from the back side of this capillary tube. Bare GP electrode was made following same fabrication process. The electrode's surfaces were cleaned by using 0.3 mM and 0.05 mM Al₂O₃ slurries consecutively. At last the electrodes got ethanolic wash and dried under nitrogen atmosphere before experiments.

2.4. Instruments and Measurements

FESEM model (Hitachi SU-8010) and TEM model (FP 5032/21 Tecnai G2 30 S-TWIN (serial No. 9921621/D934) Model No. 943205032211 made in Czech Republic) were used to analyze size and morphological aspects. A three electrode systems of the Ag/AgCl electrode was used for performing all the electrochemical measurements, Pt electrode and PrFeO₃/GP electrodes (as reference electrode, as counter electrode and working electrode respectively) by Autolab Potentiostate/Galvanostate 101 (Netherlands). The electrochemical study was carried out in 0.1(M) phosphate buffer of pH 6.0 at 25±2°C with scan rate100 mVS⁻¹ along with voltage range from 0.4V to 1.6V.

3. Results and discussion

3.1. TEM and FESEM studies GdFeO₃ nps

Surface morphology of newly prepared GdFeO₃ nps have been studied using analytical techniques like FESEM & TEM. FESEM image reveals that the newly synthesized nano material has particle size of 40
to 50 nm with cubic structure (fig.1 FESEM image of GdFeO$_3$ nps). Transmission Electron Microscope confirms the size of synthesized material. Fig. 2 illustrates the TEM picture of synthesized nano particles.

Fig. 1 FESEM image of GdFeO$_3$

Fig. 2 TEM image of GdFeO$_3$

3.2. Electrochemical studies of npGdFeO$_3$/GP and bare GP electrode
A standard $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}$ redox system was utilized to assess electrochemical property of prepared electrodes. The CV of bare GP and npGdFeO$_3$/GP electrodes for 3 mM potassium ferrocyanide solution is depicted in fig.3. As per Velasco equation, electron transfer is much efficient due lower value of peak potential separations. $\Delta E_p$ at npGdFeO$_3$/GP and bare GP electrodes have been calculated and found to be 139 mV, and 162 mV at respectively. Results indicated GdFeO$_3$/GP electrode to have higher electrochemical activity in comparison bare GP electrode with better detection limit than reported value.

3.3. Electrocatalytic oxidation of ASA at npGdFeO$_3$/GP and bare GP electrodes
The electrocatalytic aspect of ASA was investigated by CV measurements at bare GP and npGdFeO3/GP electrodes, (results shown in Fig. 4). The oxidation peak potential at npGdFeO3/GP electrodes was 1110 mV. The CV experiments were operated in the voltage range of 0.4 V to 1.6V. The oxidation current value was observed to be 15.15 µA at GdFeO3/GP and 9.8 µA at bare GP electrodes respectively and was 1.5 times more than bare GP electrode. All the results reflect quicker transfer of electron, remarkable adsorbitivity, lower detection range and excellent electro catalytic nature. All the CV experiments were carried out at scan rate of 100 mV s\(^{-1}\) using phosphate buffer of pH-6.0.

3.4. Effect of pH and rate of scan on ASA oxidation

The pH of supporting electrolyte being pivotal aspect for oxidation, effect of potential of Hydrogen on peak potential and current value of ASA were studied by CV in 0.1 M PBS of pH range 4 to 7. The peak current values of ASA increases when pH raised upto 6.0 and then decreases with further increase in pH value, which may be due to basic nature of the bio-molecules. So PBS of pH 6 was used for all
experiments performed. The effect of scan rate on the oxidation of ASA at npGdFeO$_3$/GP electrode has been examined by varying the scan rate from 0.5 mVs$^{-1}$ to 500 mVs$^{-1}$. It has been observed that peak current increases linearly with the linear increment in scan rate. (Fig. 5), indicating that the oxidation process is diffusion controlled at the surface of modified electrodes.

4. Repeatability, reproducibility & Stability of electrodes

Stability of the npGdFeO$_3$/GP electrode has been investigated by examining electrodes, electrochemical sensitivity storing at 30$^\circ$ C ± 1$^\circ$ C for 25 days. The results indicated that the sensor restored 95% of its sensing capacity. Ten times repetition of electrode response with negligible change in the sensitivity indicated its repeatability. In order to validate reproducibility five electrodes of npGdFeO$_3$/GP were fabricated by same process and were used to check sensitivity. To our delight all the electrodes showed the similar response, result depicted in fig. 6. Based of the above results it may be concluded that electrode have remarkable repeatability, reproducibility as well as stability.
5. Conclusion

Here in we report a superior GdFeO$_3$/GP sensor for detection of ASA using CV technique. The oxidation current value of GdFeO$_3$/GP electrode was observed to be 15.15 µA and 9.8 µA at bare GP electrodes and it was 1.5 times higher than bare GP electrode. The easier synthesis procedure, better sensitivity and good repeatability of newly fabricated electrodes towards detection of ASA are the high lighting features of this modified electrode. The proposed (GdFeO$_3$/GP) electrode can be effectively utilized for clinical diagnosis and in pharmaceutical industry.

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