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# Lanthanum Ortho-Ferrite ($LaFeO_3$) Nano-Particles Based Electrochemical Sensor for the Detection of Dopamine

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**Abstract:** The perovskite type lanthanum ortho ferrite nano-particles ($LaFeO_3$) based electrochemical sensor was developed and used to detect dopamine. For this work the lanthanum ortho ferrite nano-particles ($LaFeO_3$) were synthesized by combustion technique using sugar and ethanolamine with lanthanum oxide and ferric nitrate. For the characterization of newly prepared lanthanum ortho ferrite nano-particles, techniques like FESEM, and TEM were used. The crystallite size was found to be 40 to 46 nm with cubic crystal structure. To check the electrochemical properties of a modified sensor electrode ($LaFeO_3$/GP), the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were used. During the experiment, the phosphate buffer solution having pH 6.0 was employed, maintaining the scan rate 100mV$s^{-1}$ and 50mV$s^{-1}$ for cyclic voltammetry and Differential pulse voltammetry, respectively.

**Keywords:** Lanthanum ortho ferrite; Nano-particles; Cyclic voltammetry; Differential pulse voltammetry; Dopamine.



## 1. Introduction

Ventral tegmental area (VTA) of the midbrain produces, a naturally occurring biogenic compound, in the “Dargic neurons” which known for its inhibitory neurotransmitter, also involved with brain, known as Dopamine [4-(2-aminoethyle) benzene-1,2diol, DA]. During physical activities, the functioning of the central and peripheral nervous system [1, 2] was initiated by dopamine and also is responsible for emotion and endocrine system. DA may produce burning mouth syndrome [3], restless leg syndrome[4], Senile dementia, fibromyalgia[5, 6], rarely depression [7] and Parkinson’s disease[8] when its concentration is small, while the high concentration of DA, cause abnormal blood pressure and an incensement in heart rate.

For pharmaceutical industries and clinical diagnosis, the development of a useful cheap and sensitive electrode is very essential. The developed electrodes should be reliable and proficient to detect these molecules in bio fluids in the nano range. The determination of bio molecules using conventional techniques being expensive, the electrochemical approaches drew the attention of the researchers for their quick response, better selectivity, superior sensitivity and less cost. A large number of materials such as Co doped $CeO_2$ nanoparticles [9], MWCNT-$Fe_3O_4$@PDA-Ag nanocomposite [10], nitrogen doped electrochemical sensor [11] reduced graphene oxide [12], nickel telluride and cobalt telluride NPS [13], PbTe/GP electrode [14], zinc oxide [15] fabricated glassy carbon ,lanthanide-orthoferrites ($XFeO_3$/GP) [16-19] ,

Manganese ferrite & cobalt ferrite nano particle based electrode [20], urease immobilized biosensor to determine urea [21] , Indium Tin Oxide-Coated Glass Electrode [22] and Functionalized Electrodes [23] have been employed as electrode materials. Now we communicate lanthanum ortho-ferrite modified graphite paste ($LaFeO_3$/GP) electrode to detect dopamine electrochemically. So far our knowledge goes; this is the first communication on the detection of dopamine using lanthanum ortho-ferrite as an electrode modifier.

## 2. Materials and Methods

### *2.1. Chemical and Reagents.*

Procurement of $La_2O_3$ (Lanthanum oxide), $Fe(NO_3)_3 \cdot 9H_2O$ (Iron nitrate), $HNO_3$ (Nitric acid), paraffin oil and $HOCH_2CH_2NH_2$ (ethanol amine) etc. were made from Merck (India ) and graphite flakes and dopamine ($C_8H_{11}NO_2$) were procured from Sigma Aldrich, USA. Reagents being of analytical grade were used as such. Solutions were made with DD water.

### *2.2. Synthesis of lanthanum orthoferrites nanoparticles ($LaFeO_3$ nps).*

A clear solution(100 ml) of lanthanum oxide ($La_2O_3$)(1.0 mM) was taken in 500 ml beaker,ferric nitrate (1.0 mM), sugar (2.5 mM) and ethanolamine (1.7 mM) were added into it. The solution was then heated at 150 $^0$C till dryness. Blackish fluffy mass obtained was then calcined in muffle furnace at 800$^0$C for 6 hours to yield lanthanum orthoferrites nanoparticles.

### *2.3. Preparation of electrodes.*

For the working electrode ($LaFeO_3$/GP), a mixture of graphite powder and prepared lanthanum orthoferrites NPS in 4:1 ratio was mixed uniformly in a mortar and pastel by adding a few drops paraffin oil. A hallow glass tube (2mm inner diameter) is packed tightly filling with the uniform paste. The back side of capillary tube received a platinum wire inserted to have electrical contact. For bare GP only the paste of graphite powder was filled in hollow glass tube and followed the similar fabrication process. The electrode's surfaces were cleaned by using 0.3 mM and 0.05 mM $Al_2O_3$ slurries consecutively. At last rinsing of electrodes with ethyl alcohol in $N_2$ atmosphere was carried out before experimentation.

### *2.4. Apparatus and Measurements.*

Field Emission Scanning Electron Microscope (FESEM) model (Hitachi SU-8010) and Transmission Electron Microscope (TEM) model (FP 5032/21 Tecnai G2 30 S-TWIN (serial No. 9921621/D934) Model No. 943205032211 made in Czech Republic) were used for the size and morphology of synthesized nanomaterials. The electrochemical properties of the developed electrode (working electrode) were measured by using Autolab Potentiostate/Galvanostate 101 (Netherlands). Supporting electrolyte for the electrochemical study was phosphate buffer solution (0.1M) of pH 6.0 at 25±2 $^o$ C. The scan rate was maintained 100 m $VS^{-1}$ and 50 m $VS^{-1}$ along with the voltage range from 0.0V to 0.6V and 0.15 V to 0.4 V respectively for CV & DPV experiments.

## 3. Results and Discussion

### *3.1. FESEM and TEM analysis of $LaFeO_3$ nanoparticles.*

The characterizations of synthesized nanomaterials have been done using FESEM and TEM techniques. The surface morphologies of lanthanum-ortho ferrite (np-$LaFeO_3$) have uniform cubic structure with narrow size distribution. The fig 1-a, illustrates that the size of nanomaterials lies between 40-46 nm. The TEM studies are shown in fig 1-b, also supported the FESEM results.

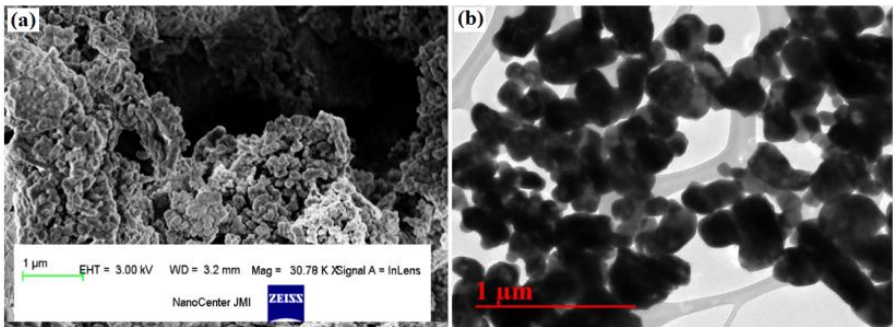


**Figure 1.** a) FESEM image and TEM image of $LaFeO_3$ nano materials.

### *3.2. Electrochemical, Scan rate and pH study at $LaFeO_3$/GP electrode.*

A standard redox system $[Fe(CN)_6]^{-4}$/ $[Fe(CN)_6]^{-3}$ was used to check the electrochemical properties of new ($LaFeO_3$/GP) electrode and bare GP electrodes. The comparative cyclic voltammograms in 3 mM $K_4[Fe(CN)_6]$ solution between bare GP and $LaFeO_3$/GP electrodes are represented in Fig. 2-a. The electrochemical band gap, particle size, surface defects, composition, capping ligand & optical band gap have a significant role in the voltammetric retaliation of the semiconducting materials.

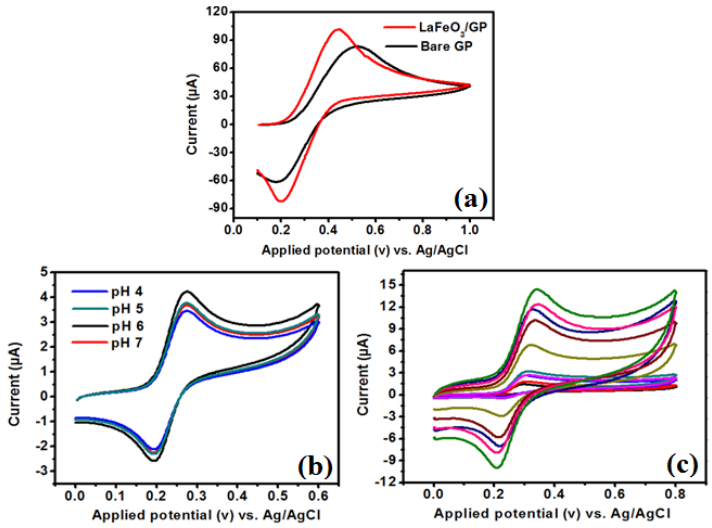


**Figure 2.** (a) Cyclic Voltammogram obtained for 3.0 mM $Fe(CN)_6^{-4}$ at $LaFeO_3$/GP and bare GP electrodes at 100 $mVsec^{-1}$ scan rate with phosphate buffer solution of pH 6.0 (b) illustrates the pH study with variation of PH from 4 to 7 and (c) Current in µA during scan rate study with making variation from 5 to 600 $mVS^{-1}$ using 100 µM concentration of dopamine.

Therefore electrochemical analysis is immensely significant. The electrons transfer rate depends on peak potential separation (ΔEp). The low value of ΔEp is a measure of faster

electrons transfer, according to Velasco equation. Fig. 2-a indicates the peak potential separation (ΔEp) at $LaFeO_3$/GP to be 240 mV and at bare GP electrode 444mV.

On the basis of the above results, it can be concluded that due to lower (ΔEp) np-$LaFeO_3$/GP electrode has a better electron transfer rate than bare GP electrode. For cyclic voltammetric response for standard redox system the oxidation peak currents at prepared electrode like $LaFeO_3$/GP and bare GP electrode were found to be 102.4 and 83.5 respectively, which was nearly 1.25 times higher than bare GP electrode.

In the electro-catalytic oxidation of DA, the effect of scan rate was studied by altering the scan rates from 5 to 600 $mVs^{-1}$ in CV technique. The linear increment in the peak current value was recorded during the experiment with enhancement in scan rate (Fig 2-c). In the electrochemical oxidation of molecules at the prepared electrode, the pH of supporting electrolyte has a principal function to play. To analyze the result of pH on the oxidation of DA, 0.1 M phosphate buffer solution (PBS) were used with varying pH range from 4.0 to 7.0. From the experiments it was observed that the peak currents of DA enhanced with rising of pH up to 6.0 and then decreased with any further increment. The maximum peak current value at np$LaFeO_3$/GP was noticed at pH 6.0. Fig. 2-b demonstrates the results. So in all experiments PBS of PH- 6.0 was used.

### *3.3. Electrocatalytic oxidation of DA at prepared $LaFeO_3$/GP electrode.*

CV and DPV techniques were employed to check electro-catalytic behavior of modified electrodes. The results for electro-catalytic sensitivity are shown in Fig.3. The cyclic voltammogram of DA at bare GP electrode, np-$LaFeO_3$/GP electrode are also shown in Fig. 3-a and 3-b.The results indicated that the oxidation peak potential at bare GP electrode and prepared electrode ($LaFeO_3$/GP) were 271 mV for dopamine.

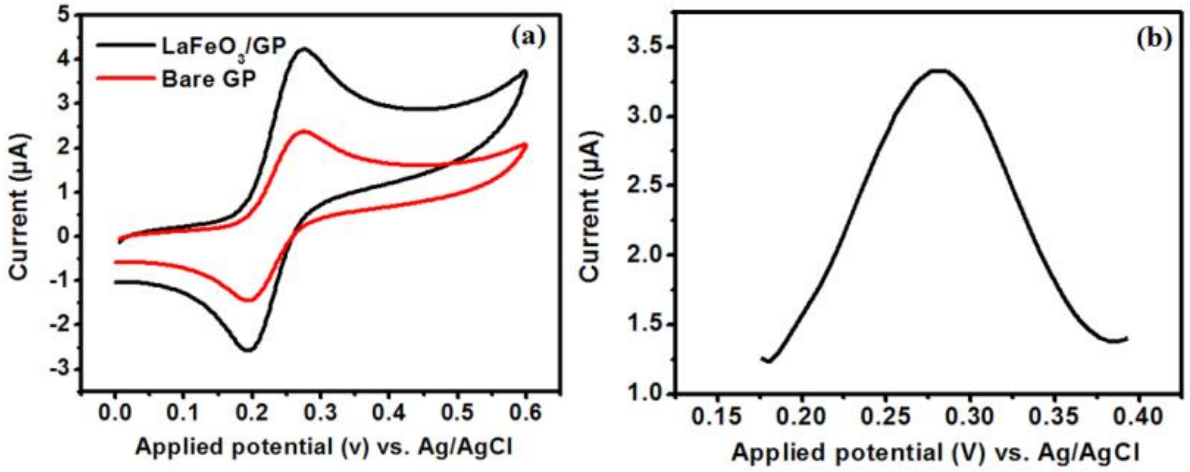


**Figure 3.** (a) represents Cyclic voltamogram and (b) diffrantial pule voltammogram at LaFeO3/GP electrode using 100 µM concentration of dopamine in 0.1(M) phosphate buffer pH 6.0 for CV, scan rate 100 $mVs^{-1}$ and for DPV, scan rate 50 $mVs^{-1}$.

### *3.4. Comparative study of different synthesized modified electrodes with ours.*

The comparison between the new electrode and previously developed electrodes (table 1), revealed that the newly developed np-lanthanum ferrite modified graphite paste electrode is surpassing to earlier in sensitivity i.e. linearity range and limit of detection.

**Table 1.** comparative study of sensitivity of praseodymium-ferrite modified graphite paste electrodes with earlier electrodes.

| Modified Electrode | detection limit (nM) | Liner range (µM) | Ref. |
|---|---|---|---|
| f-MWCNT | 800 | 3-200 | [24] |
| Pyrolytic carbon films | 2300 | 18-270 | [25] |
| PEDOT /ITO | 6770 | 1–50 | [26] |
| $LaFeO_3$/GP | 600 | 5-200 | Our Work |

*3.5. Stability, repeatability and reproducibility of electrodes.*

The modified electrode ($LaFeO_3$/GP), was stored at 25° C ± 1° C for 20 days and checked the sensing response of developed electrode and found 96% retention of sensing response, suggesting remarkable stability of the electrodes. To check the repeatability of the electrode, 6 consecutive measurements were done and were noticed to possess akin performance indicating repeatability of the electrode. For reproducibility, four electrodes were fabricated using a similar method. All four electrodes exhibited close performance supporting reproducibility. Results are shown in Fig. 4.

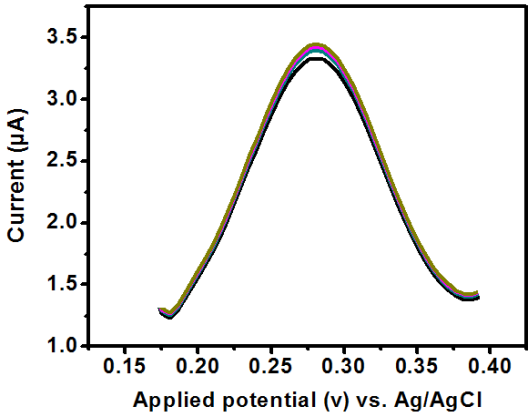


**Figure 4.** Repeatability shown by performong DPV experiment after preparing six electrodes using similar fabrication method using 100 µM concentration of dopamine in 0.1(M) phosphate buffer pH 6.0 for CV, scan rate 100 $mVs^{-1}$.

## 4. Conclusions

$LaFeO_3$ were synthesized by the combustion technique, having a particle size of 40-46 nm. The newly prepared nanoparticle based electrodes demonstrated remarkable sensitivity to detect drug/bio-molecules like dopamine in biological fluid and may be useful in clinical and pharmaceutical diagnostic.

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## Conflicts of Interest

The authors declare no conflict of interest.

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