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# Hexagonal basalt-like ceramics $La_xMg_{1-x}TiO_3$ (x = 0 and 0.5) contrived via deep eutectic solvent for selective electrochemical detection of dopamine

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## Abstract

Attributed to the increased interest in search of cost effective alternatives for electrochemical sensing materials, alkali and alkaline-earth metal oxides have seized the attention of material researchers. Herein we report the novel approach of deep eutectic solvent (DES) mediated facile solid state synthesis of pure and lanthanum doped magnesium titanate ceramics at 800°C. The unique hexagonal basalt-like structure achieved for the La-doped ceramic material showed tremendous electrocatalytic activity towards dopamine biomolecules over a wide linear detection range of 5–50µM. A remarkable limit of detection, 1.32µM was attained for La-doped magnesium titanate modified glassy carbon electrode. %RSD value of 2.04 and recovery rate of 97.95 in spiked human serum ensures its promising future as a potential, cost effective and ecofriendly electrode modifier in portable dopamine sensors for point of care human serum analysis.

## Introduction

In the past few decades, neurotransmitters have gained increased attention owing to their significant functions in mammalian central nervous system [1,2]. Dopamine (DA), is one such naturally occurring catecholamine neurotransmitter and is a metabolic precursor of epinephrine and norepinephrine [3].

Anomalies of DA levels in the body leads to certain neurological conditions such as euphoria, schizophrenia, senile dementia, epilepsy, Huntington's disease, and Parkinson's disease [4,5]. Since elimination half-life of DA in adults is approximately 2 min and infants is 4–5 min, continuous monitoring and quantification of precise amounts of DA is of more use for diagnosis and treatment purposes [6]. So far, numerous analytical methods have been explored including colorimetry, spectrometry, chromatography, capillary electrophoresis, enzyme-assisted method [7,8], and so on. However, these methods suffer undeniable drawback in terms of higher cost and laborious techniques.

Electrochemical sensing has taken over the aforementioned traditional methods with its high sensitivity, feasibility of miniaturization, fast response, easy operation, and cost effectiveness [9]. Regardless of the fact that in electrochemical analysis the oxidation products tend to stick onto the bare electrode and lower its sensitivity and selectivity [10], it has been overcome by modifying the electrode surface with suitable modifier materials such as noble metal nanoparticles, carbon based materials, conducting polymers, metal oxide composites etc [[11], [12], [13], [14]].

Haofan Sun et al. [15] put forth the electrodeposited Au nanoparticles decorated $MoS_2$ nanosheets as a potential electrode modifier for the simultaneous detection of DA analyte in the presence of ascorbic and uric acid. Padamadathil et al. [16] applied the modified Hummers' method for synthesizing partially reduced graphene oxide and modified the glassy carbon electrode (GCE) surface to achieve well-resolved detection peaks for DA. Similarly another simultaneous electrochemical detection of DA analyte was done by Hayati Filik et al. [17] which was assisted by the elecropolymerization of a diaminophenazine derivative (Safranine O) to attain poly (Safranine O) film over the GCE surface. Yixin Liu et al. [18] proposed the aid of Pd-loaded $Fe_3O_4$ nanoparticles prepared by a simple solvothermal method and successfully modified the GCE. Even in the presence of high concentrations of uric acid excellent electrocatalytic activity towards DA was observed owing to the synergetic effect between palladium and $Fe_3O_4$.

Recently perovskite ceramics are exclusively well-known for their wider zone of applications in piezo electrics, microwave dielectrics, energy storage, gas sensing, auto-exhaust catalysis, photo catalysis, solid oxide fuel cells, etc [[19], [20], [21], [22], [23]]. In general, perovskite ceramics have $ABO_3$ structural formula where A-ion can be alkali, alkaline earth and rare earth while the B-ion can be 3d, 4d, 5d transition metal ion. Among them transition and rare earth perovskites have distinguished applications in electrochemical sensing of biologically important molecules.

Yogendra Kumar et al. [24] developed nano sized cobalt ferrite $CoFe_2O_4$ and manganese ferrite $MnFe_2O_4$ via combustion method and explored the electrochemical sensing ability of the materials towards DA and paracetamol. Likewise lanthanum cobaltate $LaCoO_3$ was synthesized by Priyatharshni et al. [25] through hydrothermal method which was coated over a GCE surface and used for the simultaneous detection of DA, ascorbic acid and uric acid. Nevertheless, in spite of its varied physical and chemical properties, the potential of alkaline-earth ceramics in electrochemical sensing of biomolecules and organic pollutants remains unacquainted.

Magnesium titanate, $MgTiO_3$ (MTO) is one such alkaline-earth ceramic which falls under the perovskite family with ilmenite-like structure having R3 space group and [$MgO_6$] [$TiO_6$] complex clusters coordinating to form octahedral configuration [26]. Since the morphology, surface area, particle size, physical and chemical characteristics of the materials highly depend on the synthesis strategy it is vital to select it with utmost care.

Alike the recent synthesis techniques like electrospinning, spray pyrolysis, electrodeposition etc conventional solid state synthesis has also levitated its applicability to a wide variety of materials. This development towards superior research is assisted by upgrading the standard solvents into the next generation solvent medium, ionic liquids. Deep eutectic solvents (DESs) are a unique category of ionic liquids comprising a combo of quaternary ammonium salt and a hydrogen bond donor [27]. They have kindled the topical research society with its progressive physiochemical properties and are proven to be ecofriendly, biocompatible, less toxic, inexpensive alternative pathways for greener synthesis [28]. Depressing the eutectic temperature of a mixture comprising pure compounds than that of their individual ideal temperatures is the fundamental criterion of a DES. Preparation of a DES mixture can be through four techniques: heating, grinding, twin screw extrusion and freeze drying each with its own pros and cons [29]. They are established to be promising candidates in extraction and separation techniques. Fuel desulfurization, biphasic extraction, extraction of neonicotinoids and grape skin flavonoids, organic synthesis (aldol, cycloaddition, catalysts etc) are some exclusive milestones in the history of DESs [30]. Also, new frontiers of organic and inorganic synthesis have been markedly opened after the discovery of this solvent medium [31].

In this work, we reported the novel use of an ecofriendly DES mixture of choline chloride and urea in a 1:2 ratio to fabricate of an electrochemical dopamine sensor based on pure/La-doped magnesium titanate ceramics synthesized using a simple solid-state synthesis route. Exploration of their electrochemical detection capability towards DA analyte was investigated and validated through electro-analytical techniques like cyclic voltammetry, linear sweep voltammetry and amperometry. Real-time analysis with spiked human serum samples was also explored.

## Section snippets

## Reagents and apparatus

Dopamine was purchased from Sigma. All the chemicals choline chloride, urea, titanium dioxide, magnesium oxide, lanthanum oxide, nafion® perfluorinated resin solution, phosphate buffer solution (PBS) pH=7.4 were of analytical grade. Ultrapure doubly distilled water was used throughout the experiment.

Powder X-ray diffraction (PXRD) measurements were taken using a Bruker D8 advance powder X-ray diffractometer with CuK$\alpha$ ($\lambda$=1.5406Å) radiation at 2$\theta$ range 10–80°. Fourier transform infra-red…

## PXRD analysis

Crystal structure and phase purity of the as prepared pure MTO and La-doped MTO ceramics were studied using X-ray diffraction and their diffraction patterns are as shown in Fig. 1. Pure MTO was indexed to the perovskite ($MgTiO_3$, rhombohedral phase) with JCPDS 06–0494. In La-doped MTO the fused lanthanum dopant directed to the emergence of new additional peaks pertaining to monoclinic phased $La_2Ti_2O_7$ with JCPDS 27–1182. Diffraction peaks appeared at 2θ 33°, 36°, 40.5°, 49.5°, 54°, 57.5°, 63°,…

## Conclusions

In conclusion, for the first time in material research a simple solid-state reaction expedited with choline chloride-urea DES medium was used to render pure and lanthanum doped magnesium titanate ceramics for electrochemical sensing ability of DA biomolecules in neutral media. La-doped MTO/GCE exhibited superior sensing performance (LOD-1.32 μM) owing to its larger active surface area and porosity. Thus, the synthesized ceramic material acts as an effective replacement over other electrode…

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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> …On the other hand, La-doped BTO formed well-defined microspheres and had significant grain boundaries. Dopant lanthanum in the crystal lattice could have gathered on the grain boundaries and confined further grain growth [25]. This might have led to the reduced size of the La-doped BTO particles compared to pure BTO.…

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…The method is a precise, selective, fast and convenient analytical tool. Furthermore the method provides an opportunity to design and enhance the efficiency of materials through band gap tuning [45–48]. Picric acid is one of the prime chemicals used for the development of explosives and hence its detection is of immense importance in defense and security [49].…

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