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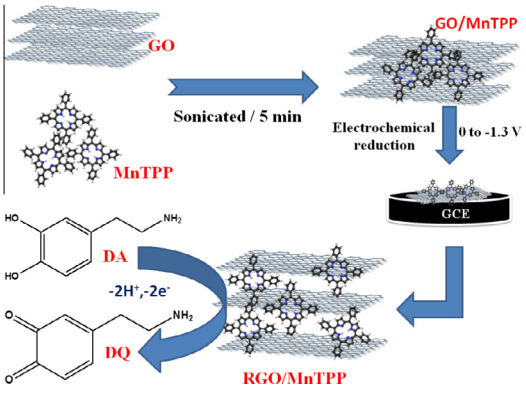
# Electrocatalytic oxidation of dopamine based on non-covalent functionalization of manganese tetraphenylporphyrin/reduced graphene oxide nanocomposite

Subramanian Sakthinathan [a], Hsin Fang Lee [a], Shen-Ming Chen [a,*], P. Tamizhdurai [b]

[a] Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC
[b] National Centre for Catalysis Research, Indian Institute of Technology, Chennai 600036, India

## GRAPHICAL ABSTRACT

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## ABSTRACT

In the present work, a reduced graphene oxide (RGO) supported manganese tetraphenylporphyrin (Mn-TPP) nanocomposite was electrochemically synthesized and used for the highly selective and sensitive detection of dopamine (DA). The nuclear magnetic resonance, scanning electron microscopy and elemental analysis were confirmed the successful formation of RGO/Mn-TPP nanocomposite. The prepared RGO/Mn-TPP nanocomposite modified electrode exhibited an enhanced electrochemical response to DA with less oxidation potential and enhanced response current. The electrochemical studies revealed that the oxidation of the DA at the composite electrode is a surface controlled process. The cyclic voltammetry, differential pulse voltammetry and amperometry methods were enable to detect DA. The working linear range of the electrode was observed from 0.3 to 188.8 μM, limit of detection was 8 nM and the sensitivity was 2.606 μA $\mu M^{-1}$ $cm^{-2}$. Here, the positively charged DA and negatively charged porphyrin modified RGO can accelerate the electrocatalysis of DA via electrostatic attraction, while the negatively charged ascorbic acid (AA) repulsed by the negatively charged electrode surface which supported for good selectivity. The good recovery results obtained for the determination of DA present in DA injection samples

* Corresponding author.
*E-mail address:* smchen78@ms15.hinet.net (S.-M. Chen).

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and human pathological sample further revealed the good practicality of RGO/Mn-TPP nanocomposite film modified electrode.



## 1. Introduction

Dopamine (DA) is a very important catecholamine neurotransmitter which plays a significant role in the function of renal, hormonal and central nervous system [1,2]. It implicates in many human behaviors such as, reward, cognition, motor function, motivation, and also it plays a critical role in learning and memory [3,4]. Deficiency of DA may cause several diseases such as schizophrenia and Parkinson's disease [5,6]. So the sensitivity and selective detection of DA is highly important. Many methods have been developed for DA detection including capillary electrophoresis [7], liquid chromatography [8], calorimetric method [9] chemiluminescence [10,11], fluorescence [12], electrochemical [13], etc. [14–19]. Among these detection methods, recently electrochemical methods have received more attention due to its advantages of selectivity, low-cost, portability, easy handling and less-time consuming. Unfortunately, the ascorbic acid (AA) and uric acid (UA) usually interfere with the DA sensing, because of their similar oxidization potential with DA. Therefore, the development of suitable electrode materials is an important for the selective and discriminative detection of DA [20–24]. Graphene, a two-dimensional (2D) $sp^2$ bonded one atom thick nanomaterial has been widely used as an electrode material in electrochemical sensors. Graphene has interesting properties such as, high surface-to-volume ratio, excellent electrical conductivity and electrocatalytic activity. Moreover, graphene has large π-electron structure and it can electocatalyze the analytes via π-stacking type adsorption. Besides, its edges also provide additional catalytic sites which is ideal for electrocatalytic applications. Recently graphene has been working as a sensor for the DA because the π–π interaction between the DA molecule and graphene [25–28]. Graphene oxide (GO), an oxygenated derivative of graphene is the most preferable starting precurser for the preparation graphene based composites. Generally, during composite formation GO will be reduced to graphene via reduction during composite formation. GO will be reduced to graphene to restore the $sp^2$ network using different methods such as chemical, electrochemical and thermal methods [29]. The chemical reduction method involved excessive toxic chemicals as a reducing agents such as, hydrogen sulfide, hydrazine, $NaBH_4$, dimethylhydrazine, hydroquinone, and aluminium powder. However, the chemically reduction method encounter important drawbacks such as, use of toxic chemicals, lack of control in film thickness, formation of nitrogen impurities, requires long time, and involves exothermic reaction. In contrary, electrochemical methods are best alternative to chemical methods due to its simple, inexpensive, efficient, low-cost and environmentally friendly approach. Also, electrochemical methods are easy to control film thickness and for the preparation of stable films without any further treatment. Therefore, in the present work we have used facile electrochemical reduction method for the preparation of reduced graphene oxide/manganese tetraphenylporphyrin (RGO/MnTPP) nanocomposite [30,31].

Porphyrin is a biomedical and synthetically interesting compound that includes many biological representative such as heme, chlorophyll, myoglobins and cytochromes. They are used in photosynthesis and transport mechanism in living organisms [32]. Porphyrin is a macro cyclic conjugated molecule which has an extensive system of resonance π electrons. The porphyrin coordinate with many metal ions (such as, Co, Cu, Fe, Mn, and Zn) to form stable metalloporphyrin complexes, which are widely used in research due to special physiological activity. Moreover, it has excellent electron transfer, energy conversion, and nonlinear optical limiting properties [33–35]. It has been used as electrocatalysts toward oxidation and reduction reactions of related life process. Generally, they were functionalized with carbon nanomaterials by either covalent or non-covalent methods and used for any kinds of applications. Comparatively, non-covalent functionalization approach has advantages over covalent functionalization since it avoids destruction and preserving their unique properties without damage [36–38]. Designing graphene supported metal porphyrins and metal phthalocyanines for electrochemical sensing applications is our lab's continuous on-going research work. For instance, we are working on cobalt (II) phthalocyanine (CoPc) [39], cobalt phthalocyanine/iron phthalocyanine (CoPc)/(FePc) composites [40], iron phthalocyanine (FePc) [41], nickel tetrasulfonated Phthalocyanine (NiTsPc) [42], copper tetraphenylporphyrin (CuTPP) [43], etc. Recently, we have reported the preparation of reduced graphene oxide supported copper tetraphenylporphyrin for the detection of DA. However, chemical method has several disadvantages, therefore herein we have described simple and fast electrochemical method for the preparation of RGO supported MnTPP.

The main objective of the present work is to develop a simple electrochemical method to prepare RGO/MnTPP for the sensitive and selective determination of DA. Here, Mn-TPP molecules were assembled and flattened on the RGO surface via non-covalent stacking interactions and the conjugation of metal/porphyrin is enlarged. The flattening of porphyrin molecules can further reduce the distance between RGO and metal porphyrin molecules which further enhanced stacking interaction. The RGO/Mn-TPP nanocomposite exhibits the high electrocatalytic activity for DA. The RGO/Mn-TPP nanocomposite prepared by environmentally friendly approach. Furthermore, DA detection very low level 8 nM and the electrode sensitivity 2.606 $\mu A\ \mu M^{-1}\ cm^{-2}$ also increasing than that of the our previous CuTPP/CRGO work, So the RGO/Mn-TPP can be an excellent material for the electrochemical detection of DA, and also shows high sensitivity, low level detection and selectivity toward DA detection.

## 2. Experimental

### 2.1. Materials and methods

Graphite powder (1–2 μm), propionic acid, benzaldehyde, pyrrole, methanol, zinc acetate, potassium ferricyanide, potassium ferrocyanide, uric acid and ascorbic acid all other chemicals received from Sigma–Aldrich. Dopamine hydrochloride injection (easy dopa injection 1.6 mg $ml^{-1}$) purchased from Aldrich, were diluted with PBS prior to the analysis of real sample. Sulfuric acid ($H_2SO_4$), hydrochloric acid (HCl) was purchased from Merck Chemical. All the purchased chemicals used as an analytical grade and the purified condition. Human urine sample was obtained from two healthy men and the sample was stored in the refrigerator at 4 °C. The supporting electrolyte medium was used for pH 7 it was prepared by using 0.05 mol $L^{-1}$ $Na_2HPO_4$ and $NaH_2PO_4$. The prepared buffer solution pH adjusted by 0.5 mol $L^{-1}$ $H_2SO_4$ or HCl and 2 mol $L^{-1}$ NaOH. Double distilled water was used to prepare all solutions in the whole experiment. Prior to the each experiment the electrolyte was purchased by nitrogen ($N_2$) for deoxygenation.