



# Nanostructured $\beta$ -tricalcium Phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) Based Electrochemical Sensor for Detection of Methyl Parathion and Mercury (II) Ions

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In this work, we have fabricated a new electrochemical sensor based on  $\beta$ -tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) nanoparticles (NPs) modified glassy carbon electrode (GCE) for the selective nonenzymatic determination of methyl parathion and mercury (II) ions independently.  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) NPs were prepared by chemical precipitation method and structural and morphological properties were investigated by XRD, FTIR, and SEM. The electrochemical behavior of MP and mercury ( $\text{Hg}^{2+}$ ) ions were investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques using  $\beta$ -TCP/GCE. The modified electrode exhibited excellent electrocatalytic activity towards both the MP and Hg over a wide linear range from 0.15 to 141  $\mu\text{M}$  and 1–381  $\mu\text{M}$  with the lowest detection limits of 88 and 136.4 nM respectively. The sensor has high selectivity towards MP and Hg in the presence of major interfering compounds such as 3-nitrophenol, 4-nitrophenol, 4-aminophenol, catechol, hydroquinone and heavy metals such as lead, cadmium and arsenic. Applicability of the fabricated sensor for detection of MP and Hg (II) ions has been tested in tap water by standard addition method.

**Keywords:**  $\beta$ -Tricalcium phosphate, electrochemical sensor, methyl parathion (MP), mercury ion, environmental applications and catalysis

## INTRODUCTION

Organophosphorus pesticides (OPs) are extensively used as insecticides in the field of agriculture to protect crops, seeds and to get high yield with high quality (Mulchandani et al., 2001; Obare et al., 2010). However, these pesticides are neurotoxic which can cause several diseases in both humans and animal (Silva et al., 2004; Chuan et al., 2015). Methyl parathion (MP) is a type of nitro aromatic organophosphorus pesticide which is widely used to prevent agricultural losses by controlling pests and insects. It is used prevalently due to its cost effectiveness and high insecticidal activity (Niazi and Yazdanipour, 2007; Sanghavi et al., 2012). MP's ability to bio-accumulate and its low solubility means that it can easily be adsorbed on the surface of water and soil which could result in various problems to our eco-system. Moreover, high dosages of MP lead to inhibition of acetyl cholinesterase activity in the brain and leads to disturbances in normal neuron transmission (Yang et al., 2008; Thota and Ganesh, 2016). More than 100 thousand people die every year due to MP pesticide driven contamination of food and drinking water. Therefore, with the spotlight on public health, there

is a need to develop reliable, highly sensitive and easily operable methods for the monitoring of MP concentration in the environment and food items. Various methods such as spectroscopic, chromatographic techniques like high performance liquid chromatography (Cappiello et al., 2002; Hyötyläinen et al., 2004; Berijani et al., 2006; Moinfar and Hosseini, 2009; Hassan et al., 2010) and electrochemical methods (Shulga and Kirchoff, 2007; Liang et al., 2012) have been used for determination of MP. Among them, electrochemical techniques were most suitable for monitoring the MP concentration, because of its high sensitivity, selectivity and low-cost (Liu and Lin, 2006; Du et al., 2011). Though there are electrochemical sensors for MP determination, these methods depend heavily on enzymes (Mulchandani et al., 1999; Liu and Lin, 2006; Gong et al., 2009; Du et al., 2011; Hossain et al., 2011; Li et al., 2011; Du et al., 2012; Ge et al., 2013). These enzyme based electrochemical sensors are usually less favored for practical usage because they suffer from many disadvantages such as high cost, instability, denaturation, difficulty in getting pure form of enzymes, subsequent storage problems and short life time. In order to overcome these problems, novel enzyme free sensor devices for methyl parathion detection such as MWCNTs-PAAM based composite (Zeng et al., 2012), carboxylic acid functionalized single walled carbon nanotubes-cyclodextrin ( $\beta$ -SWCNTs-CD) (Yao et al., 2014), mono-6-thio-cyclodextrin-gold nanoparticles-single walled carbon nanotubes SHCD/AuNPs/SWCNTs (Fu et al., 2015), gadolinium hexacyano ferrate-graphene nanosheets (GdHCF/GNs) (Li et al., 2014) zirconia nanoparticles (ZrO<sub>2</sub>NPs) (Parham and Rahbar, 2010) have been developed.

Heavy metal ions such as cadmium, lead, arsenic, mercury are major contributors to environmental pollution, albeit in very low concentrations, because of their undesirable involvement in many natural and industrial applications. Mercury and its compounds are highly toxic and when they accumulate in human organs such as liver, heart muscle, and brain. They can easily interact with protein and enzymes which, in turn, results in the inactivation of some important cell functions in our body leading to various diseases like kidney dysfunction, central nervous system disorders, even death at high exposure (Harris et al., 2003; Triunfante et al., 2009; Bodo et al., 2010; Johri et al., 2010). As a result, attention has been directed to the determination of mercury ions in foodstuff and pharmaceutical products and the environment. Traditional analytical tools for the determination of mercury ions include atomic absorption spectroscopy (AAS) (Kenawy et al., 2000; Pohl, 2009) and inductively coupled plasma mass spectrometry (ICP-MS) (Caroli et al., 1999; Silva et al., 2009). Compared to the above-mentioned techniques, electrochemical methods offer several advantages in terms of cost, simplicity and quickness. Moreover, in electrochemical techniques, different voltammetric methods can be employed for mercury detection (Aragay and Merkoç, 2012). Several reports are available for electrochemical determination of mercury ion; PdO/NP-CPE (El Aroui et al., 2014), EDTA/CPE (Moutcine and Chtaini, 2018), EDTA-PANI/SWCNTs/SS (Deshmuk et al., 2018), Chloroplatinum (II) complex-MWCNTs paste electrode (Mdisa et al., 2017) and Av-HA/GCE (Kanchana et al., 2015).

Calcium phosphate (Ca/P) bioceramics are well known bioactive compound and are used in surgical fields for orthopedic and dental implants, because of their excellent osteoconductivity. Hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)), octacalcium phosphate (Ca<sub>8</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>·5(H<sub>2</sub>O)), tricalcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), calcium hydrogen phosphate dihydrate (CaHPO<sub>4</sub>·2H<sub>2</sub>O), dicalcium phosphate anhydrous (CaHPO<sub>4</sub>), tetracalcium phosphate (Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O) and amorphous calcium phosphate (Ryu et al., 2002) are different crystalline calcium phosphates that have been applied in many biological mineralization processes. Among them, tricalcium phosphate has been given great attention and it is widely used as an ideal temporary scaffold for bone implant and dental repair material, because of its close chemical resemblance to biological apatite present in human hard tissues. Tricalcium phosphate can be divided into three forms based on its thermal stability namely  $\alpha$ ,  $\beta$ - and  $\alpha'$ -phases. Of these,  $\alpha$ -TCP is hydrolysable while  $\beta$ -TCP is a stable material with superior properties such as non-toxicity, antigenicity, non-carcinogenicity, high biodegradability and thermal stability (Tadayyon et al., 2003). Though with relatively poor performance in terms of the lowest detection limit and linear range, the  $\alpha$ -TCP modified carbon paste electrode (TCP/CPE) was used for the determination of Pb<sup>2+</sup> by electrochemical method (Chourak et al., 2016).

The present work reports the fabrication of an enzyme free electrochemical sensor for methyl parathion determination and mercury ion detection using  $\beta$ -tricalcium phosphate modified GCE. The fabricated electrode was employed for determination of MP and mercury (II) ions in tap-water samples.

## MATERIALS AND METHODS

### Reagents

Methyl Parathion was purchased from Sigma Aldrich, Mercuric Chloride, Calcium Nitrate tetra hydrate and di-ammonium hydrogen phosphate were purchased from Merck Private Limited, Mumbai. All other chemicals were of analytical reagent grade and used without any further purification. 0.1 M of Phosphate buffer solution was prepared from Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> (Merck, Mumbai) and the pH was adjusted to seven and five for MP and Hg respectively by adding 0.1 M HCl. De-ionized water was used throughout the experiments.

### Apparatus

Electrochemical measurements were carried out on CHI 609D workstation. A three-electrode cell system was used with a modified glassy carbon electrode as the working electrode. An Ag/AgCl was used as the reference electrode and a platinum wire electrode as the counter electrode. All experiments were carried out at room temperature. Cyclic voltammograms (CVs) were acquired at a scan rate of 50 mVs<sup>-1</sup> in 0.1 M phosphate buffer containing various concentrations of methyl parathion and HgCl<sub>2</sub> individually. The structure and morphology of the  $\beta$ -TCP were characterized by powder X-ray powder diffraction (XRD) using a XPERT-PRO diffractometer with Cu K $\alpha$  radiation (1.5406 Å) at 40 kV and Field emission scanning electron

microscopy (FE-SEM) using FEG Quanta. Fourier transform infrared (FTIR) observations were recorded from 400 to 4,000  $\text{cm}^{-1}$  at room temperature with a Shimadzu-IR-Affinity by KBr pellet technique.

## Synthesis of $\beta$ -Tricalcium phosphate

$\beta$ -Tricalcium phosphate was prepared by a simple chemical precipitation method. Initially, calcium nitrate tetrahydrate [ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] powder and di-ammonium hydrogen phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ] solution were mixed with constant stirring to get homogenous solution. The solution turned white color turbid immediately which was made transparent by adding phosphate ion solution into calcium. Subsequently, ammonium solution ( $\text{NH}_4\text{OH}$ ) was added drop wise in the above mixture to maintain the pH 8.0. Stirring was continued for 2<sup>o</sup>h, and the precipitate was allowed to settle overnight, then filtered, dried and finally calcinated at 700°C in ambient atmosphere.

## Electrode Preparation

Glassy carbon electrodes (3 mm dia) were polished with 0.05 mm alumina powder on polishing cloth, rinsed thoroughly with deionized water between each polishing step, sonicated and dried at room temperature. These electrodes were modified by drop casting method. Here, tricalcium phosphate nanoparticles were dispersed into deionized water (5<sup>o</sup>mg/ml<sup>-1</sup>) by ultrasonication for about 30 min to get a stable and uniform suspension. Typically, 10  $\mu\text{L}$  of this  $\beta$ -TCP suspension was drop casted onto the GCE and the water was allowed to evaporate at room temperature in air.

## RESULT AND DISCUSSION

### Characterization of Synthesized Powder

Powder XRD pattern of the pristine  $\beta$ -Tricalcium phosphate sample is shown in (Figure 1A). The XRD pattern corresponds well with that of the standard  $\beta$ -TCP crystallites (ICDD PDF Card No-09-0,169) indicating that the product obtained is mainly composed of the  $\beta$ -TCP form of calcium phosphate with rhombohedral structure. No characteristic peaks

of impurities such as calcium hydroxide and calcium phosphates were observed. Crystallite size was calculated by the Debye-Scherrer formula ( $D = K\lambda/\beta/2\cos\theta$ ) where  $\lambda$  is the wavelength,  $\beta/2$  is the full width at half maximum (FWHM),  $\theta$  is the diffraction angle, K is the shape factor constant. The average crystallite size of  $\beta$ -TCP was calculated as 28 nm after several measurements.

(Figure 1B) shows the FT-IR spectra of pure  $\beta$ -TCP samples. The IR characteristic peaks of phosphate groups appeared between 900 and 1,160  $\text{cm}^{-1}$ . In particular, the peak around at 924  $\text{cm}^{-1}$  confirms the formation of high crystalline  $\beta$ -tricalcium phosphate phase. A small peak at 728  $\text{cm}^{-1}$  is attributed to the presence of  $\text{PO}_4^{4-}$  group, which is characteristic of calcium pyrophosphate phase. The peaks between 900 and 1,200  $\text{cm}^{-1}$  represent the stretching vibration of phosphate ions. The presence of two characteristic bands at around 568 and 604  $\text{cm}^{-1}$  is due to the asymmetric stretching vibration of  $\text{PO}_3^{3-}$  (Supplementary Figure S1A,B) shows FE-SEM micrographs of the  $\beta$ -TCP at two different magnifications confirm the formation of homogeneously distributed elongated rod-shaped nanoparticles.

### Electrochemical Investigation of Methyl Parathion

Cyclic voltammetry was used to investigate the electrochemical behavior of MP at the  $\beta$ -TCP modified GCE in PBS (pH 7.0) at a scan rate 50 mV/s (Supplementary Figure S2A). shows the CVs of 50  $\mu\text{M}$  MP at bare GCE (curve a) and a  $\beta$ -TCP/GCE (curve b) respectively. Noticeably, a small defined oxidation wave and large reduction peak appeared for both bare and modified GCEs. The large cathodic peak shows the reduction of nitrogroup in MP to 2-phenylhydroxylamine. During the reverse scan, a small anodic peak indicates the conversion of hydroxylamine to nitrobenzene. When compared with bare GCE, the  $\beta$ -TCP/GCE exhibited significantly enhanced redox reaction which could partly be attributed to the efficient adsorption property of tricalcium phosphate nanoparticles. No obvious peak was observed on the  $\beta$ -TCP/GCE in the absence of MP. A sharp reduction peak appeared after incubation of 50  $\mu\text{M}$  of MP in electrolyte

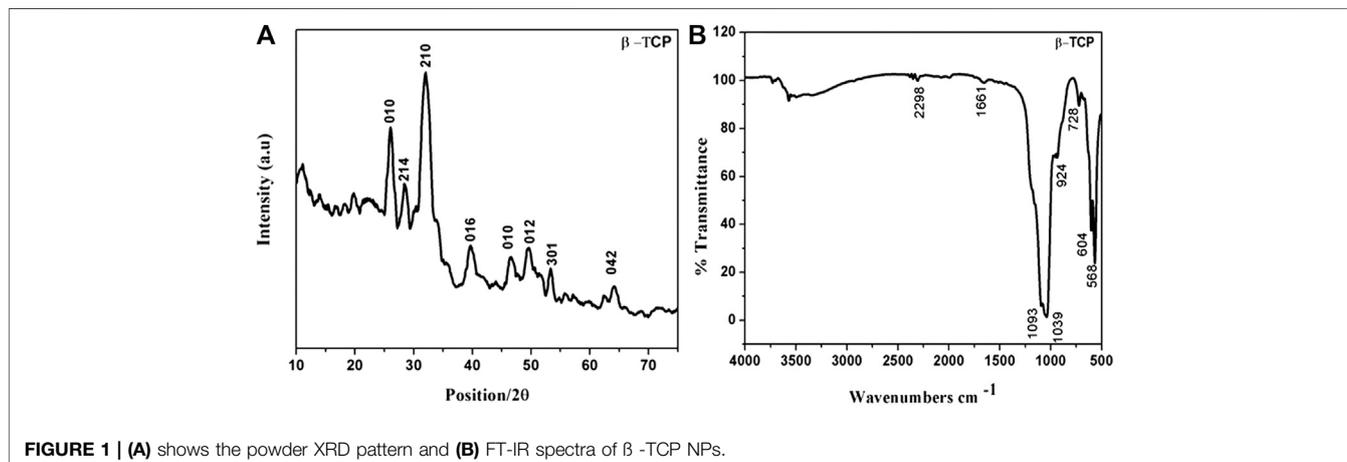


FIGURE 1 | (A) shows the powder XRD pattern and (B) FT-IR spectra of  $\beta$ -TCP NPs.

solution in (**Supplementary Figure S2B**). These results suggest that the  $\beta$ -TCP catalyzes the reaction and enhance the reduction of MP through electron transfer at the electrode-electrolyte interface.

(**Supplementary Figure S2C**) shows the effect of scanning rate on cyclic voltammograms of 50  $\mu\text{M}$  MP at the  $\beta$ -TCP/GCE in PBS at pH 7.0. The reduction peaks increase linearly with the increase of scan rates from 10 to 100  $\text{mVs}^{-1}$  and exhibit a linear relation to the square root of the scan rate, which implies that the redox reaction of MP at the  $\beta$ -TCP/GCE is a surface adsorption-controlled process. The above results also demonstrate that the proposed sensor facilitates electron transfer towards MP sensing. The methyl parathion has different electrochemical behaviors in different electrolytes. The effects of electrolytes, such as HCl, phosphate buffer, acetate buffer, and  $\text{KNO}_3$ , on reduction peak currents of MP were studied and the results show that the MP has the best electrochemical responses in 0.1 M PBS with the appearance of well defined cathodic peaks with the lowest background current.

(**Supplementary Figure S2D**) shows the cyclic voltammograms of 50  $\mu\text{M}$  of MP at  $\beta$ -TCP/GCE in 0.1 M PBS at different pH values. The pH was varied from four to nine by the addition of HCl or NaOH in PBS electrolyte. The best peak current with lowest background current appeared for pH 7.0. At lower low pH values, the peak current is reduced possibly due to the immobilization of MP on the electrode surface and/or dissolution of  $\beta$ -TCP in acidic medium. When the pH is higher than 7.0, peak current decreased and the shape of the peak is changed due to the lack of protons  $\text{H}^+$ . Hence, we have chosen pH value as 7.0 for all subsequent measurements.

## Determination of Methyl Parathion by SWV

Electrochemical determination of MP at  $\beta$ -TCP/GCE was realized by square wave voltammetric technique in 0.1 M PBS (pH 7.0) (**Figure 2A**). shows the voltammograms recorded during addition of aliquot from the stock of solution methyl parathion. It was noted that the cathodic peak current increases linearly with the increasing concentration of MP from 0.15 to 141  $\mu\text{M}$ . A linear relationship

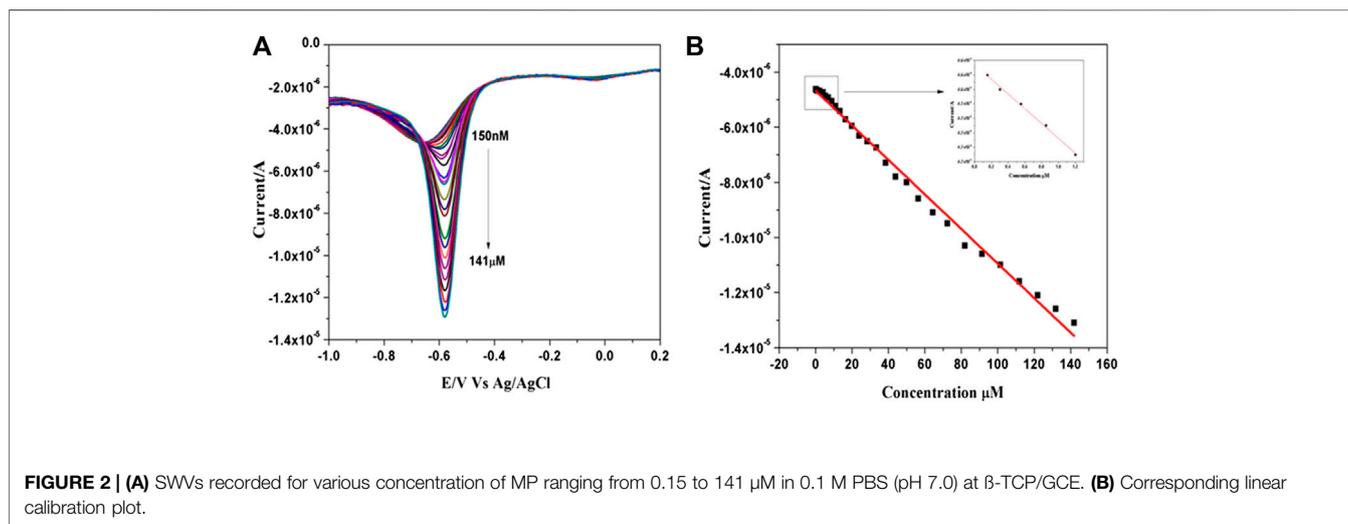
between the cathodic peak current  $i_{pa}$  ( $\mu\text{A}$ ) and concentrations  $C$  ( $\mu\text{M}$ ) of MP has been deduced as  $i_{pa}$  ( $\mu\text{A}$ ) =  $-4.6229C_{MP}$  ( $\mu\text{M}$ ) – 5.09 ( $R^2 = 0.99518$ ) (**Figure 2B**). The lowest limit of detection (LOD) was estimated as 88 nM and the results are compared with the literature values (**Supplementary Table S1**). This significant LOD over a wide linear range could be attributed to the intrinsic porous nature, efficient adsorptivity and improved electrocatalytic ability of the  $\beta$ -TCP nanoparticles.

## Selectivity, Reproducibility and Stability Studies for Methyl Parathion Sensor

A significant benefit of  $\beta$ -TCP NPs is its good selectivity towards MP sensing by avoiding and discriminating the interference of several isostructural compounds. Here we have evaluated the spirited test for selectivity by square wave voltammetry technique (**Supplementary Figure S3**). shows an interference study of MP sensor in the presence of 100 fold excess of co-existing phenolic compounds such as four-aminophenol, nitrophenol isomers, hydroquinone, catechol, and some other compounds like nitrite,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . The presence of these competing molecules and ions did not have an obvious influence on the current response of MP on the  $\beta$ -TCP/GCE. The results demonstrate that the  $\beta$ -TCP sensor can be used directly for detecting MP even in complex solutions. To characterize the reproducibility of the  $\beta$ -TCP/GCE, 15 consecutive measurements were made for 50  $\mu\text{M}$  MP at the same electrode. The results showed a relative standard deviation (RSD) of 2.97%, revealing that the  $\beta$ -TCP modified GCE had good reproducibility. The stability of the  $\beta$ -TCP/GCE sensing device was also examined by measuring CV peak current of 50  $\mu\text{M}$  MP after storing the electrode for 10 days in a refrigerator. The  $\beta$ -TCP/GCE retained 91% of the original values, demonstrating that the sensing device had better long-term stability.

## Real Sample Analysis

The analytical application of the fabricated sensor was tested in tap water and vegetable samples by the standard addition method. Methyl parathion stock solution was added into tap



water in 0.1 M PBS (pH 7.0) and the measurements were done at  $\beta$ -TCP/GCE without any prior treatment and the results are presented in **Supplementary Table S2**. It can be noticed that fabricated sensor exhibits a good recovery in the range of 96–98% for MP determination in tap water. Similarly, square wave voltammograms were recorded for *Momordica Charantia* extract (colloquially known as bitter gourd) in the presence of various concentration of MP in 0.1 M PBS and the results are shown in **Supplementary Table S2**. Here also, the  $\beta$ -TCP/GCE revealed highest percentage of recovery (90–100%) indicating its suitability for real sample analysis.

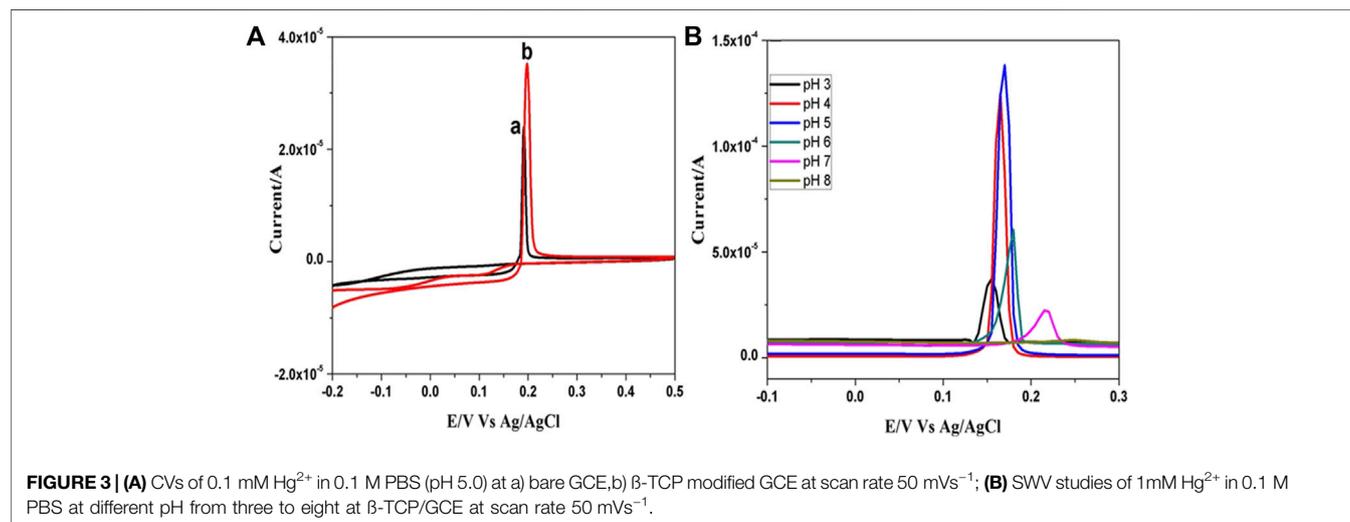
## Electrochemical Detection of Mercury ( $\text{Hg}^{2+}$ ) at $\beta$ -TCP/GCE

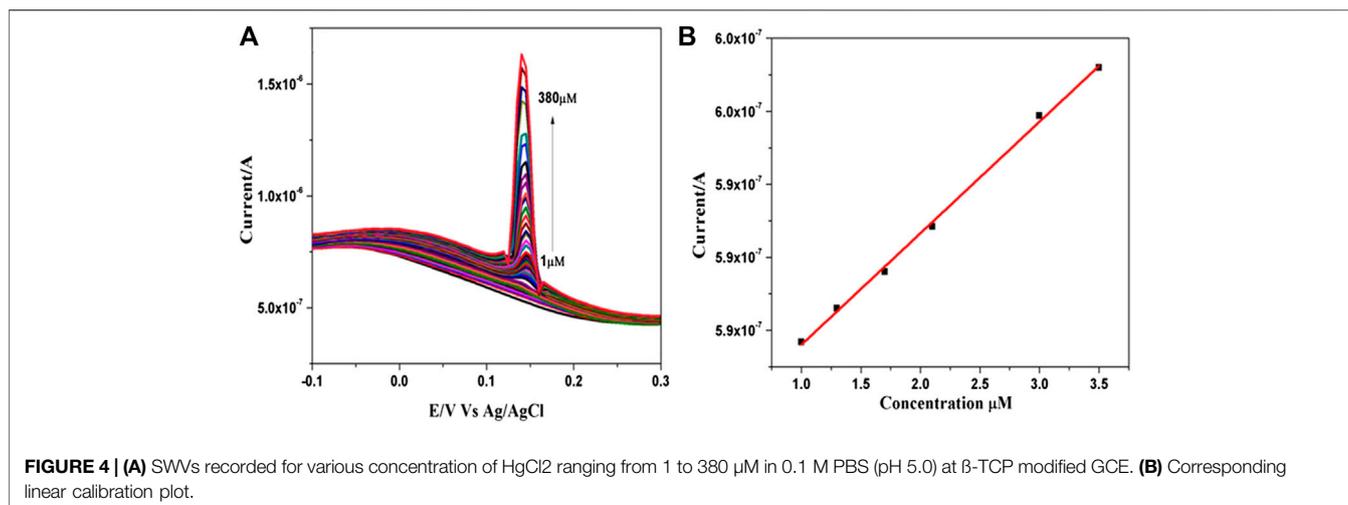
(**Figure 3A**) shows the cyclic voltammetric behavior of mercury ( $\text{Hg}^{2+}$ ) obtained in 0.1 M PBS (pH 5.0) containing 0.1 mM  $\text{HgCl}_2$  solution at bare GCE and  $\beta$ -TCP modified GCE at the scan rate of  $50 \text{ mVs}^{-1}$ . A sharp anodic oxidation peak is observed at 0.197 V corresponding to oxidation of metallic mercury ( $\text{Hg}_0 \rightarrow \text{Hg}_2^{++} + 2e^-$ ) in both bare and  $\beta$ -TCP modified GCE. The peak current ( $i_{pa}$ ) values of bare GCE and  $\beta$ -TCP/GCE were found to be 23.3 and  $35.2 \mu\text{A}$  respectively. There is a reasonable increment in the oxidation peak current of TCP/GCE when compared to that of bare GCE which reveals that the  $\beta$ -TCP has good catalytic activity. The porous nature of TCP leads to the high adsorption of mercury ion on the surface of the electrode which promotes high electron transfer at the electrode-electrolyte interface without requiring any pre-concentration time as reported in literature (Kanchana et al., 2015). Mercury ( $\text{Hg}^{2+}$ ) ions are known to have different electrochemical behaviors in different electrolytes. The effects of electrolytes, such as HCl, phosphate buffer, acetate buffer, and  $\text{KNO}_3$ , on oxidation peak currents of  $\text{Hg}_2^{++}$  were studied and the results show that the  $\text{Hg}^{2+}$  ions have the best electrochemical responses in 0.1 M PBS. When the measurements were performed in this electrolyte, well defined peaks with the lowest background current were obtained.

The effect of pH on the oxidation of mercury at the  $\beta$ -TCP/GCE in 0.1 M PBS containing 1 mM  $\text{HgCl}_2$  solution was investigated by SWV studies (**Figure 3B**). The anodic peak current is strongly dependent on the pH of the solution with the maximum current observed at pH 5.0. At higher pH values ( $>5.0$ ), the peak current decreased rapidly and the peak shape was also destroyed which could be attributed to the high participation of  $\text{OH}^-$  resulting in the hydrolysis of  $\text{Hg}^{2+}$  to form mercury hydroxide. Similarly, SWV measurements at lower pH values ( $<5.0$ ) yield lower oxidation current due to the dissolution of  $\beta$ -TCP in high acidic medium. Based on these observations, pH 5.0 was chosen as the optimum value for the supporting electrolyte.

Square wave voltammetry (SWV) was used to examine the sensitivity of the fabricated electrode towards the detection of  $\text{Hg}^{2+}$  ions (**Figure 4A**). shows the SWV response of the  $\beta$ -TCP/GCE to the successive addition of mercury in 0.1 M PBS at pH 5.0. The electrode exhibited a rapid and sensitive response to the change of mercury concentration and an obvious increase in anodic peak current upon successive addition of mercury. Further, the current increased linearly with increasing  $\text{Hg}^{2+}$  concentration over the range of 1–380  $\mu\text{M}$  and a linear relationship between the anodic peak current  $i_{pa}$  ( $\mu\text{A}$ ) and concentrations  $C$  ( $\mu\text{M}$ ) of  $\text{Hg}_2^{++}$  have been deduced as follows;  $i_{pa} (\mu\text{A}) = 0.576 C \text{ Hg}_2^{++} (\mu\text{M}) + 7.638$  ( $R^2 = 0.99784$ ) (**Figure 4B**). The lowest detection limit was found to be 136 nM and is comparable with the results obtained from many sensors (**Supplementary Table S3**) as reported in the literature. The present experiments demonstrated that it is possible to determine  $\text{Hg}^{2+}$  using  $\beta$ -TCP modified GCE without surface fouling of the electrode for repeated measurements. These results confirmed that  $\beta$ -TCP modified electrode provides a good electro catalytic activity towards the detection of heavy metal mercury.

Tap water samples were selected for real sample analysis using the standard addition method. The developed sensor (TCP/GCE) was applied to test mercury ion in tap water samples. Standard stocks mercuric chloride solution was added into tap water and





analyses were done without any prior treatment. The results are presented in (Supplementary Table S4). It is obvious from the table that a good recovery could be obtained. Thus, the proposed sensor can be used to determine mercury ions in environmentally polluted water samples.

## CONCLUSION

A novel and simple strategy for the sensitive detection of methyl parathion and heavy metal mercury individually using the β-TCP/GCE is presented in this paper for the first time. The results confirm that in the case of unmodified bare GCE, the voltammograms of both MP and mercury (II) ion exhibit just a small peak current, whereas the peak current is significantly enhanced on β-TCP/GCE. Well-defined reduction peak for MP and enhanced oxidation peak current for mercury (II) ion have been obtained owing to the excellent catalytic activity of β-TCP NPs. In addition, the β-TCP/GCE electrode exhibited good reproducibility, long-term stability, and high sensitivity without using any specific electron transfer mediator or any other surfactant. The modified electrode shows the extraordinary selectivity for determination of methyl parathion and mercury without interference of high concentration of co-existing molecules. Furthermore, the practical application of the modified electrode was demonstrated in tap water samples by using SWV method with satisfactory results.

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## DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## AUTHOR CONTRIBUTIONS

NS carried out the nanoparticles synthesis, experiments, analysed the XRD, FTIR, SEM, electrochemical behavior and wrote the paper; CS supervised the whole work and revised the paper.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fnano.2021.632652/full#supplementary-material>.

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