

## Electrochemical Fabrication of Nano TiO<sub>2</sub> Bilayer Film Modified Electrode and Electroanalytical Applications

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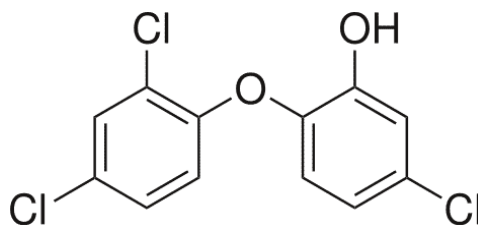
Direct detection of triclosan-methyl has been carried out at nano TiO<sub>2</sub> bilayer film (nano TiO<sub>2</sub>-IR 786 iodide dye) modified glassy carbon electrode (GCE). Nano TiO<sub>2</sub> bilayer film modified GCE was fabricated by manually coating of TiO<sub>2</sub> nanoparticles and following with the electrochemical deposition of IR-786 iodide dye. The nano TiO<sub>2</sub> bilayer film modified GCE electrochemically active and stable in various buffer solutions. The proposed film successfully detects the triclosan-methyl in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11). Further it also detects the triclosan in real sample (tooth paste). The sensitivity and the detection limit of the nano TiO<sub>2</sub> bilayer film modified GCE for the detection of triclosan-methyl was found as 21  $\mu\text{A mM}^{-1}$  and 5  $\mu\text{M}$ . Further the sensitivity and detection limit for triclosan detection in the real sample at the nano TiO<sub>2</sub> bilayer film modified GCE was found as 63  $\mu\text{A mM}^{-1}$  and 1  $\mu\text{M}$ .

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**Keywords:** Nano TiO<sub>2</sub>, IR-786 iodide dye, electrochemical deposition, triclosan, real sample, differential pulse voltammetry.

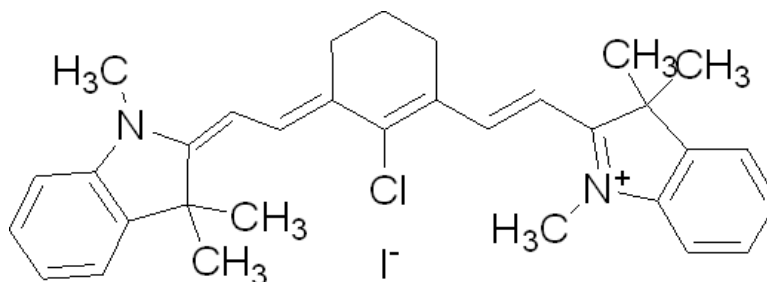
### 1. INTRODUCTION

Triclosan (2, 4, 4'-trichloro-2'-hydroxydiphenyl ether) known as polychlorophenol organic compound possess the antifungal and antibacterial properties (scheme-1). It was found as effective for the reduction of bacteria. Therefore, it has been used as an active ingredient in soaps, deodorants, shaving creams, tooth pastes and mouth washes etc., Presence of triclosan in the environment is toxic for the aquatic bacteria. Utilization of triclosan in house hold products will introduce the dioxin-like compounds in the surface of waters which found as toxic for the human health. Residual wastes containing triclosan show adverse effects in fish from the downstream water, in waste water processing plants and in the human metabolism.



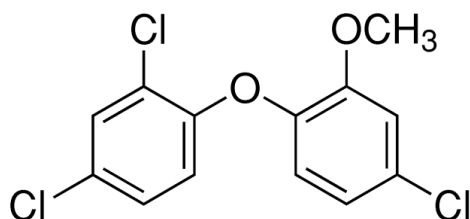
**Scheme 1.** Structural formula of triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether)

Various analytical methods have been employed for the detection and determination of triclosan. For example, gas chromatographic determination of triclosan in the waste water of a slaughterhouse [1], voltammetric detector for liquid chromatography: determination of triclosan in rabbit urine and serum [2], measurement of triclosan in water using a magnetic particle enzyme immunoassay [3] were reported. In electroanalytical chemistry, film modified electrodes were found to be simple, cost effective and suitable for the detection and determination of various types of chemical and biochemical compounds [4-12]. Detection and determination of triclosan were carried out at the modified electrodes. For example, electrochemical behavior of triclosan at a screen-printed carbon electrode and its voltammetric determination in toothpaste and mouth rinse products [13], electrochemical determination of triclosan at a mercury electrode [14], electrochemical inactivation of triclosan with boron doped diamond film electrodes [15], electrostatic accumulation and determination of triclosan in ultrathin carbon nanoparticle composite film electrodes [16], microwave activation of electrochemical processes: high temperature phenol and triclosan electro-oxidation at carbon and diamond electrodes [17], chemically surface-modified carbon nanoparticle carrier for phenolic pollutants for extraction and electrochemical determination of benzophenone-3 and triclosan [18], nanofibrillar cellulose-chitosan composite film electrodes for the competitive binding of triclosan [19], reconstituted cellulose films for the accumulation and detection of triclosan [20], at multiwall carbon nanotube film [21], electropolymerized molecularly imprinted polymer [22], analysis of various types of disinfectants using differential pulse voltammetry [23], voltammetric determination in waste water and in personal care products [24] were reported for the detection of triclosan. These reports validate that the electrochemical method is more suitable, simple and economically cheaper for the detection and determination of triclosan.



**Scheme 2.** Structural formula of IR-786 iodide dye (2-[2-[2-Chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethenylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-

Metal oxide nanoparticles are well known for their active electrochemical applications [25-29]. In this, nanoTiO<sub>2</sub> particles play special nature for the electrode surface modifications and sensing applications [30, 31]. In this report, we have attempted to fabricate film modified glassy carbon electrode (GCE) for the detection and determination of triclosan compounds. Pretreated GCE has been modified with nano TiO<sub>2</sub> particles following with the electrochemical deposition of IR-786 iodide dye (scheme-2) [32] for the nano bilayer film fabrication process.



**Scheme 3.** Structural formula of triclosan-methyl (2,4,4'-trichloro-2'-methoxydiphenyl ether)

Fabricated bilayer film was successfully employed for the detection of triclosan compounds such like triclosan-methyl (scheme-3) in lab sample and triclosan (scheme-1) in real samples. The bilayer film successfully shows the electrochemical oxidation signals for the detection of triclosan methyl and triclosan in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11).

## 2. MATERIALS AND METHODS

### 2.1. Reagents

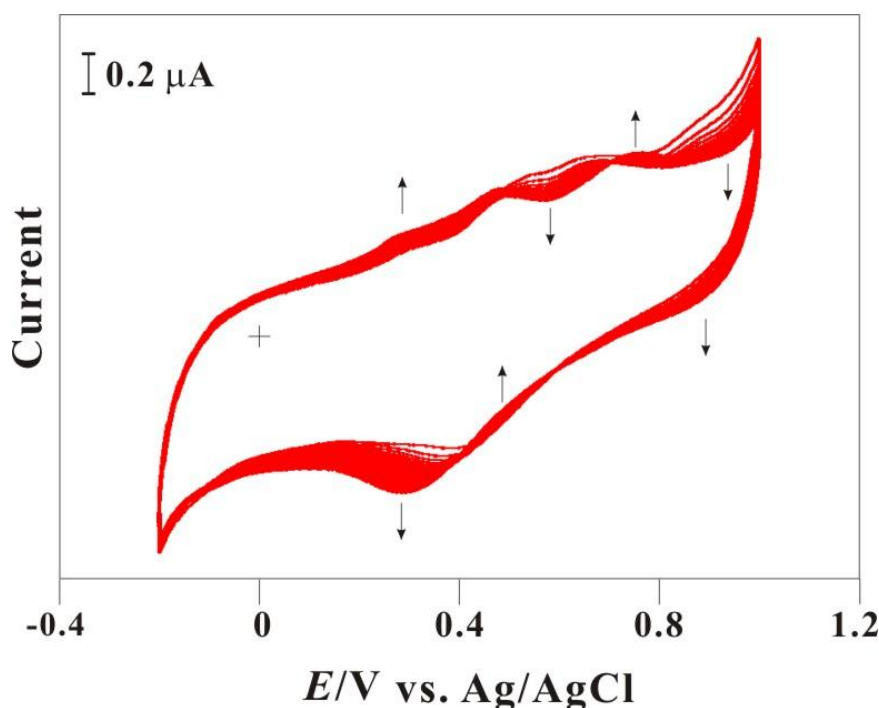
IR-786 iodide dye ((2-[2-[2-Chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethylindolium iodide)) and triclosan-methyl were purchased from Sigma-Aldrich (USA). All the other chemicals used were of analytical grade (99 %). Nano TiO<sub>2</sub> colloid was purchased from ever light chemicals (Taiwan). Double distilled deionized water was used to prepare all the experimental solutions. Pure nitrogen gas was passed through all the experimental solutions. For the triclosan electrocatalysis, 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11) has been used as buffer solution. Triclosan real sample analysis has been carried out using commercially available tooth paste samples were purchased from local convenient store.

### 2.2. Apparatus

All the electrochemical experiments were performed using CHI 410a potentiostat (CH Instruments, USA). Glassy carbon electrode (GCE) and indium tin oxide coated glass electrode (ITO) were used for the electrochemical fabrication of IR-786 iodide dye-nano TiO<sub>2</sub> film. Conventional three electrode system has been used which consists of IR-786 iodide dye-nano TiO<sub>2</sub> film modified GCE as

working electrode, Ag/AgCl (saturated KCl) as reference and platinum wire as counter electrode. XRD analysis has been carried out using XPERT-PRO (PANalytical B.V., The Netherlands). The AFM images were recorded with multimode scanning probe microscope (Being Nano-Instruments CSPM-4000, China).

### 2.3. Fabrication of nano TiO<sub>2</sub> bilayer film



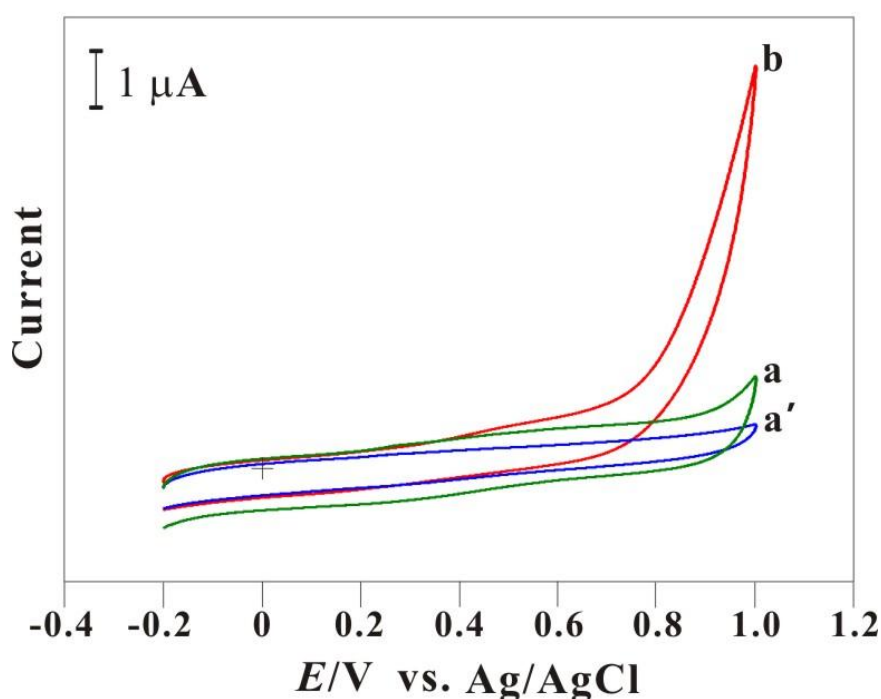
**Figure 1.** Consecutive cyclic voltammograms of IR-786 iodide dye electrodeposition at the nano TiO<sub>2</sub> modified GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> (pH 1) containing  $1 \times 10^{-4}$  M IR-786 iodide dye at the scan rate of 0.1 V/s for sixty cycles (scan range 1 to -0.2 V).

Bare GCE was polished with BAS polishing kit using 0.05  $\mu\text{m}$  alumina powder and further washed very well and ultrasonicated using deionized distilled water. At first 1 gram of Nano TiO<sub>2</sub> colloid was dissolved in 10 ml of distilled water (5 ml) and ethanol mixture (5 ml) and kept in ultrasonication for one hour. Next the pretreated GCE was coated with 4  $\mu\text{L}$  of nano TiO<sub>2</sub> colloid by manual coating and dried in air condition. Further the nano TiO<sub>2</sub> modified GCE was immersed in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution (pH 1) containing  $1 \times 10^{-3}$  M IR-786 iodide dye for the electrochemical deposition process. The iodide dye has been electrodeposited on the nano TiO<sub>2</sub> modified GCE by using the cyclic voltammetry (Figure 1). Here the continuous scan cycles was applied in the range of 1 to -0.2 V at the scan rate of 0.1 V/s for sixty cycles. Finally, the nano TiO<sub>2</sub> bilayer film was carefully washed with deionized water, dried and employed for the further electrochemical analysis. For the AFM analysis, the nano TiO<sub>2</sub> bilayer film has been prepared on ITO by following the above mentioned method, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of nano TiO<sub>2</sub> bilayer film

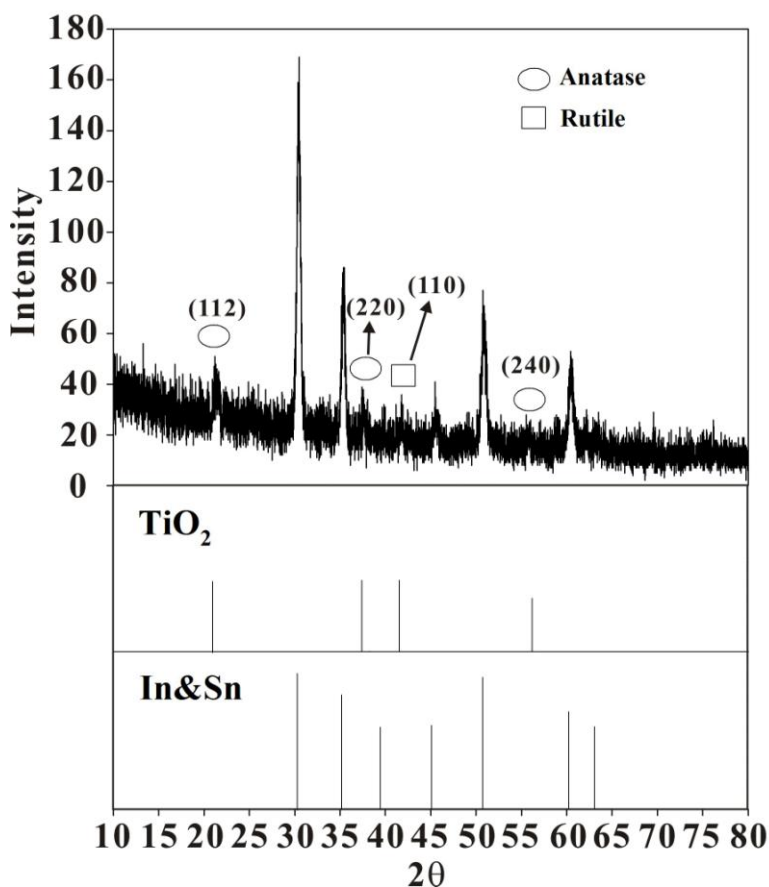
Figure-1 shows the electrochemical deposition of IR-786 iodide dye on nano TiO<sub>2</sub> particles modified GCE. Here the electrochemical deposition window falls in between 1 and -0.2 V for sixty cycles. Electroreduction process starts from 1 V and sharp reduction peak obviously appears at 0.39 V and increases for the continuous cycles and shifts to more negative potential. In the remaining oxidation cycle, obvious peaks appear at 0.48 and 0.76 V, respectively. For the continuous cycling process, all the peaks were increasing clearly. This result clearly shows the electrochemical deposition of IR-786 iodide dye.



**Figure 2.** CV response of (a) nano TiO<sub>2</sub> modified, (b) nano TiO<sub>2</sub> bilayer film (nano TiO<sub>2</sub>-IR 786 iodide dye), and (a') bare GCE in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11).

To validate the presence of both nano TiO<sub>2</sub> and IR-786 film, modified GCE was employed for the background studies in pH 11 Na<sub>2</sub>CO<sub>3</sub> (0.1 M). Figure-2 curve (a) shows the only nano TiO<sub>2</sub> particles modified GCE and curve (b) shows the nano TiO<sub>2</sub>-IR-786 film modified GCE and curve (a') shows the bare GCE background current response in pH 11 Na<sub>2</sub>CO<sub>3</sub>. Here curve (b) shows the sharp increase in the current at 1 V comparing with only TiO<sub>2</sub> and bare GCE. This happens because the electrodeposited IR-786 film shows the sharp anodic current at 1 V. Based on this result we conclude that both the nano TiO<sub>2</sub> and IR-786 film present on the electrode surface. Different scan rate studies have been done for the nano TiO<sub>2</sub> bilayer film in pH 11 Na<sub>2</sub>CO<sub>3</sub> (Fig not shown). From the lower scan

rate 0.01 to 1 V/s it the background current responses were clearly increasing. This shows that the fabricated bilayer film found to be electrochemically active in pH 11  $\text{Na}_2\text{CO}_3$ .

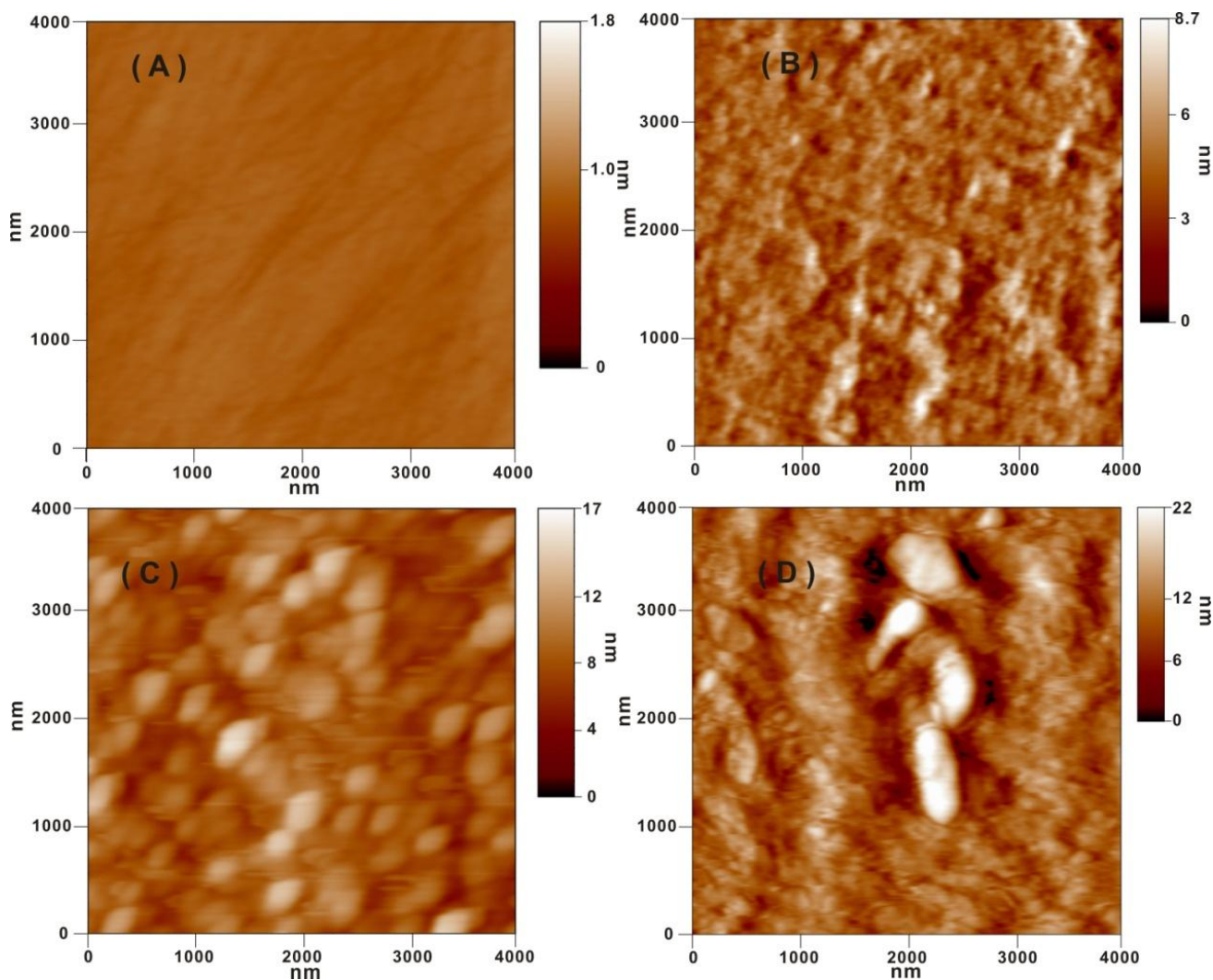


**Figure 3.** XRD pattern of nano  $\text{TiO}_2$  modified ITO.

X-ray diffraction analysis has been employed for the detailed examination of nano  $\text{TiO}_2$  particles. The nano  $\text{TiO}_2$  modified ITO has been employed for the XRD analysis. Figure-3 shows the XRD pattern of only nano  $\text{TiO}_2$  modified ITO. Here the nano  $\text{TiO}_2$  particles XRD diffraction patterns were found as 112, 220, 110 and 240 with anatase and rutile phases, respectively. Further detailed surface morphological analysis has been carried out using AFM.

Figure-4 (A) shows AFM 2D scan image of the unmodified bare GCE surface, (B) shows the only IR-786 iodide dye electrodeposited GCE surface, (C) shows the only nano  $\text{TiO}_2$  particles coated GCE and (D) shows the nano  $\text{TiO}_2$  bilayer film modified GCE. Comparing the Figures-4 (B) and (C) with Fig (A), we can clearly see the electrodeposited IR-786 dye and manually coated nano  $\text{TiO}_2$  particles on the GCE surface. Here the electrodeposited IR-786 was found as a non uniform thin layer on the electrode surface. At the same time, only nano  $\text{TiO}_2$  particles (Fig. 4(C)) displays like spherical shaped with the average diameter of 83 nm. For nano  $\text{TiO}_2$  bilayer film it appears totally different from both Fig-(B) and (C). It appears like a thin film with some globular particles on the surface. Here the nano  $\text{TiO}_2$  particles were not as much visible as like Fig-4(C) because the electrochemical deposition

of IR-786 film which entirely covers the coated nano TiO<sub>2</sub> particles and only few nano particles visible at the electrode surface.



**Figure 4.** AFM two dimensional view of (A) bare, (B) IR-786 iodide dye electrodeposited, (C) nano TiO<sub>2</sub> modified, and (D) nano TiO<sub>2</sub> bilayer film (nano TiO<sub>2</sub>-IR 786 iodide dye) modified GCE.

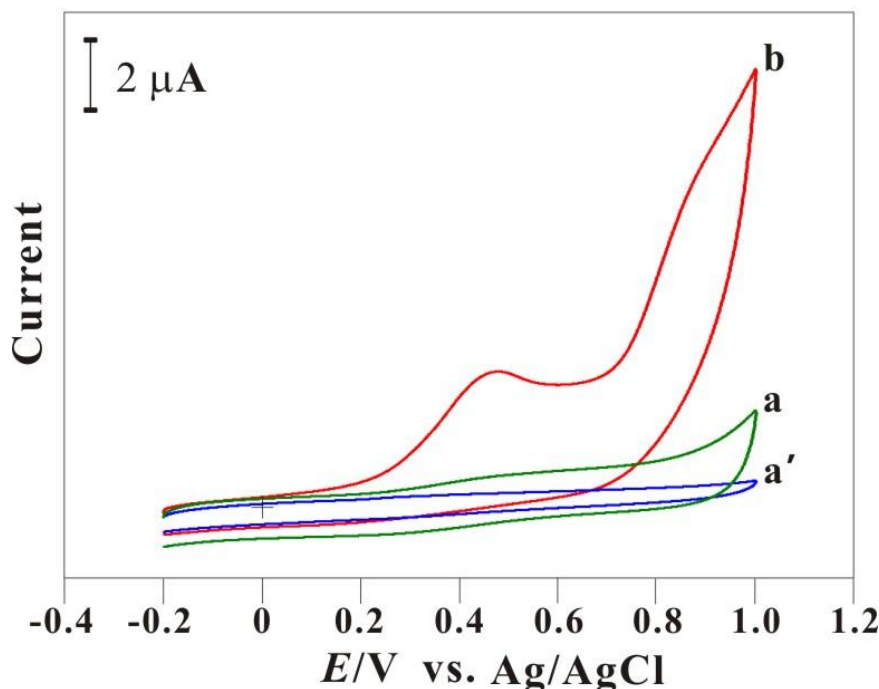
**Table1.** AFM analysis

AFM parameter	IR-786 modified GCE	Nano TiO <sub>2</sub> modified GCE	Nano TiO <sub>2</sub> bilayer film modified GCE
Average height (nm)	1.06	1.32	2.22

Further Table-1 shows the average height of the bare, IR-786 film, nano TiO<sub>2</sub> particles and nano TiO<sub>2</sub> bilayer film. Comparing with bare, IR-786 film and nano TiO<sub>2</sub> particles modifications the nano TiO<sub>2</sub> bilayer film’s height was found as high. This result clearly validates the presence of both layers on the electrode surface. Finally, the above results clearly explicate the surface morphology of the nano TiO<sub>2</sub> bilayer film.

### 3.2. Electrochemical detection of Triclosan-methyl at Nano TiO<sub>2</sub> bilayer film modified GCE

Electrochemical detection of triclosan-methyl has been carried out at the nano TiO<sub>2</sub> bilayer film modified GCE in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11). Here pH 11 Na<sub>2</sub>CO<sub>3</sub> buffer solution has been employed for the lab and real sample analysis. At first, cyclic voltammetry has been employed to validate the electrochemical activity of the nano TiO<sub>2</sub> film for the triclosan-methyl detection. Figure-5 curve (b) shows the CV response for triclosan-methyl detection at the nano TiO<sub>2</sub> bilayer film modified GCE.



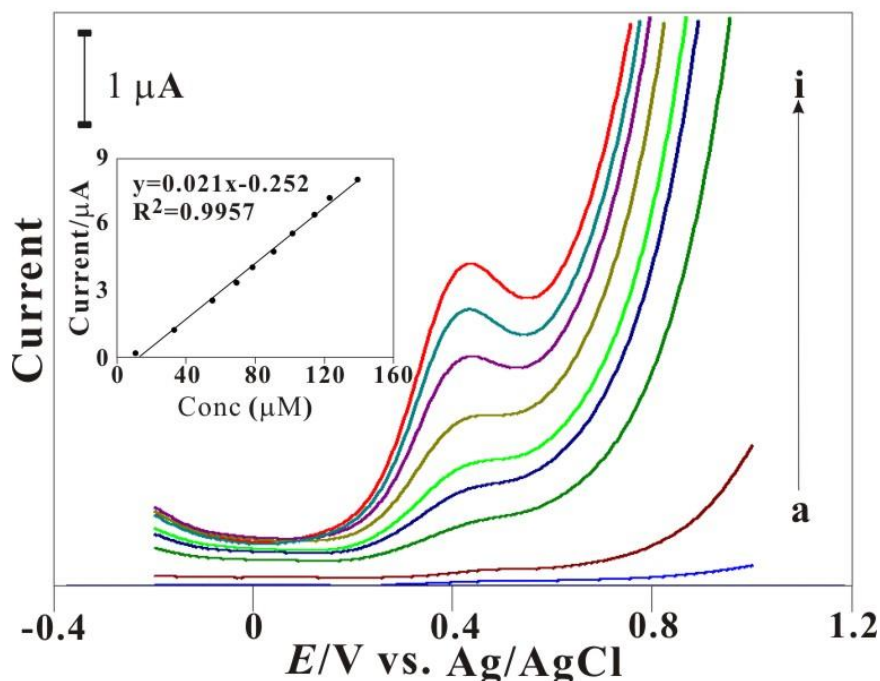
**Figure 5.** CV response of (a) nano TiO<sub>2</sub> modified (b) nano TiO<sub>2</sub> bilayer film (nano TiO<sub>2</sub>-IR 786 iodide dye) modified, and (a') bare GCE for the detection of triclosan ( $1 \times 10^{-4}$  M) in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11).

Figure-5 curve (a) is the CV response for triclosan-methyl detection at only nano TiO<sub>2</sub> modified GCE and curve (a') is the bare GCE response for the triclosan-methyl detection. Comparing the CV response of curve (b) with (a) and (a') we can clearly see the result that nano TiO<sub>2</sub> bilayer film shows the obvious electro oxidation current signal at 0.45 V. The bare and only TiO<sub>2</sub> modified GCE shows null response for the detection of triclosan-methyl in pH 11 Na<sub>2</sub>CO<sub>3</sub>. Here the enhanced electro oxidation current was observed at nano TiO<sub>2</sub> bilayer film modified GCE. This may be due to the presence of electrodeposited IR-786 iodide dye which actively electrocatalyzes the triclosan methyl, respectively. Based on this result, we conclude that the proposed film holds the capacity to detect triclosan-methyl. For the detailed electrochemical analysis, DPV technique has been employed.

Figure-6 shows the differential pulse voltammograms for triclosan-methyl detection at nano TiO<sub>2</sub> bilayer film modified GCE. For the consequent additions of triclosan-methyl in pH 11 Na<sub>2</sub>CO<sub>3</sub> the nano TiO<sub>2</sub> bilayer film shows obvious oxidation peak current at 0.44 V and the electro-oxidation



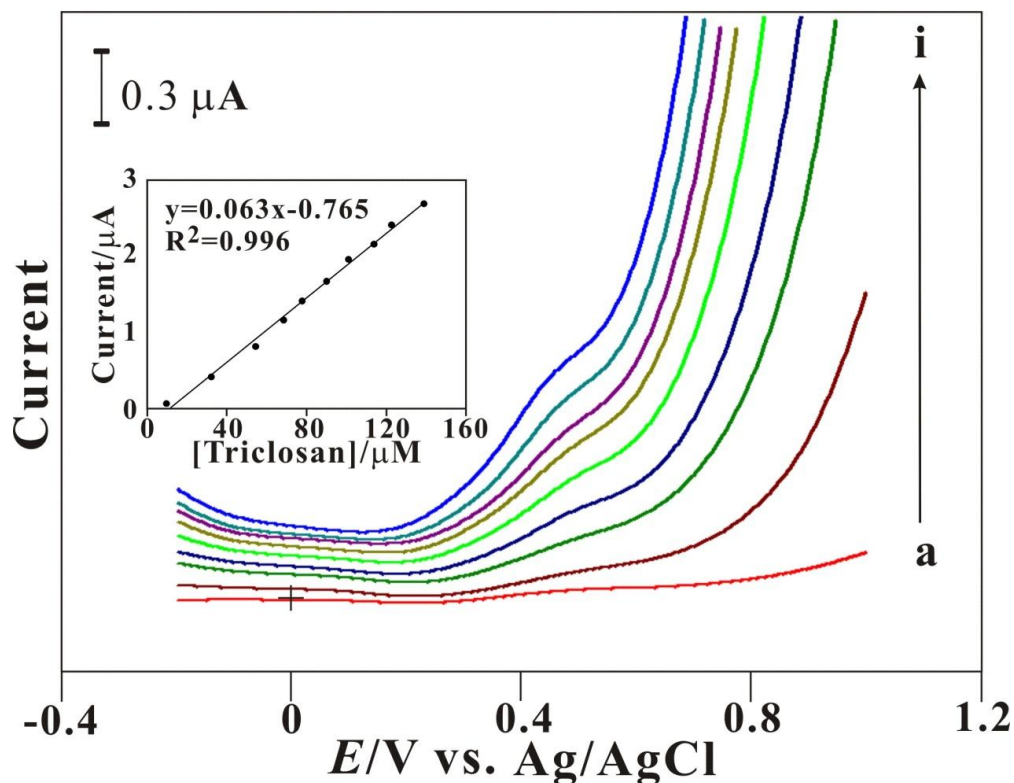
peak currents were linearly increasing. Further the linear range of detection for triclosan-methyl at this film was found as 10 to 139  $\mu\text{M}$ . Figure-6 inset shows the current vs. calibration plot for the detection of triclosan-methyl. From the calibration plot the linear regression equation obtained as  $y = 0.021x - 0.252$ ,  $R^2 = 0.9957$ . Furthermore, the sensitivity and detection limit for the nano  $\text{TiO}_2$  film for triclosan-methyl detection were found as  $21 \mu\text{A mM}^{-1}$  and  $5 \mu\text{M}$ .



**Figure 6.** DPV responses for the detection of triclosan-methyl at the nano  $\text{TiO}_2$  bilayer film (nano  $\text{TiO}_2$ -IR 786 iodide dye) modified GCE (in  $0.1 \text{ M Na}_2\text{CO}_3$  (pH 11)). Triclosan methyl additions were in the range of (a-i; 10, 32, 55, 69, 78, 90, 101, 114 and  $139 \mu\text{M}$ ). Inset shows the current vs. concentration plot for the triclosan-methyl detection.

**Table 2.** Comparison table for the detection of triclosan

S. No.	Type of Electrode	Method	pH	Potential	Linear Range	Detection limit	Ref
1.	Screen printed carbon electrode	DPV	10	0.45 (V)	$1.2 \mu\text{M} - 1.0 \text{ mM}$	-	13
2.	Mercury electrode	DPV	7	-450 (mV)	$2.5 - 60 \mu\text{g L}^{-1}$	$1.9 \mu\text{g L}^{-1}$	14
3.	Ultrathin carbon nanoparticle composite modified ITO film	CV	9.5	0.6 (V)	$0.5 - 50 \mu\text{M}$	-	16
4.	Cellulose-PDDAC modified GCE	CV	9.5	-	$10^{-6} - 10^{-3} \text{ mol dm}^{-3}$	-	20
5.	MWCNT film modified GCE	DPV	7.0	-	$50 \mu\text{g L}^{-1} - 1.75 \text{ mg L}^{-1}$	57 nM	21
6.	GCE	DPV	9.9	0.56 (V)	$17.3 - 103.6 \mu\text{M}$	$7.4 \mu\text{M}$	23
7.	Nano $\text{TiO}_2$ bilayer film modified GCE	DPV	11	0.45 (V)	$10 - 139 \mu\text{M}$	$1 \mu\text{M}$	This work



**Figure 7.** DPV responses for the detection of triclosan in real samples at the nano TiO<sub>2</sub> bilayer film (nano TiO<sub>2</sub>-IR 786 iodide dye) modified GCE (in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11)). Triclosan additions were in the range of (a-i; 10, 32, 55, 69, 78, 90, 101, 114 and 139 μM). Inset shows the current vs. concentration plot for the triclosan detection.

Further analysis has been focused on the determination of triclosan in real samples. Most of the tooth paste samples, mouth rinsing solutions contain triclosan in certain percentages. Therefore, here we have selected tooth paste sample (120 g contain 0.25 % triclosan) which has been purchased from local convenient store. Real sample has been prepared in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11). Figure-7 shows the DPV response of nano TiO<sub>2</sub> bilayer film for the detection of triclosan in the real sample. For each and every additions of real sample, the nano TiO<sub>2</sub> bilayer film modified GCE shows electro oxidation current increase at 0.45 V. Here the oxidation peak for triclosan is not as much visible like triclosan-methyl. This may be due to the presence of other chemical compounds in the tooth paste sample. However, for each addition, it shows the electro-oxidation current increase clearly at 0.45 V. Further the sensitivity and the detection limit at nano TiO<sub>2</sub> bilayer film for the detection of triclosan was found as 63 μA mM<sup>-1</sup> and 1 μM. Fig. 7 inset shows the current vs. calibration plot for the detection of triclosan from real sample. From the calibration plot the linear regression equation for the detection of triclosan was found as  $y = 0.063x - 0.765$ ,  $R^2 = 0.996$ . From these lab sample and real sample examinations, it shows that the nano TiO<sub>2</sub> bilayer film modified GCE well suits for the detection of triclosan. Table-2 shows the comparison study of triclosan detection based on previous literature reports. From this table we can notice that DPV technique has been employed mostly for the detection of triclosan. Various types of electrodes like glassy carbon electrode, screen printed carbon electrode,

mercury electrode were used for the detection of triclosan. Further in film modified electrodes, carbon nanoparticle composite film, cellulose composite films and multi wall carbon nanotubes modified electrodes have been utilized for the detection of triclosan. Most of these electrodes have been employed in alkaline pH condition for the detection of triclosan. Also, in 0.4 - 0.6 (V) potential ranges, most of the electrodes detect the triclosan. Comparing with these methods, the nano TiO<sub>2</sub> bilayer film also detects the triclosan in real sample at the 0.45 V (in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH 11)), with sufficient linear range (10 - 139 μM), sensitivity (63 μA mM<sup>-1</sup>), and detection limit (1 μM). Also, this type film preparation method is very easy and convenient one. These discussions clearly confirm the advantage of the proposed film and the capacity to detect the triclosan in real samples, respectively.

#### 4. CONCLUSION

Nano TiO<sub>2</sub> particles coated IR-786 iodide dye bilayer film successfully fabricated on GCE and ITO. This bilayer film was found as electrochemically active in various buffer solutions. Electrochemical detection and determination of triclosan-methyl and triclosan were successfully carried out at this bilayer film. This film overcomes the interference signals of other chemical compounds present in commercial tooth paste sample and shows only the triclosan detection signals. Also, the sensitivity and detection limit of the film falls within the satisfactory limits for the detection and determination of Triclosan. Therefore, this type of bilayer film could be employed for the fabrication of prototype electrochemical sensors for the detection of triclosan compounds.

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