

Investigation of electrocatalytic effect on azine electrolyte using TiO₂, ZnS loaded TiO₂ modified glassy carbon and platinum electrode

Arun V and Sankaran KR*.

Department of Chemistry, Annamalai University, Annamalainagar, Tamil Nadu, India.

*Corresponding Author: E-Mail: professorskrs60@gmail.com

Received: 20 July 2015, Revised and Accepted: 28 July 2015

ABSTRACT

Fluorenone unsymmetrical azines have been synthesized in the presence of acid catalyst sulphated-titania (TiO₂-SO₄²⁻) and they are characterized by FT-IR and ¹H spectral analysis. Surface modifier materials titanium dioxide and zinc sulfide loaded titanium dioxide are synthesized. Glassy carbon and its modified electrodes are characterized by SEM. Electrocatalytic effect of electrolytes (azine + dimethylformamide (DMF) + (TBAP) tetrabutylammonium perchlorate) have been investigated using glassy carbon electrode (GCE), Nafion coated titanium dioxide GCE (GCNCTME), Nafion coated Zinc sulfide loaded titanium dioxide GCE (GCNCZDTME), Platinum electrode (PtE), Nafion coated titanium dioxide PtE (PTNCTME) and Nafion coated Zinc sulfide loaded titanium dioxide PtE (PTNCZDTME) in cyclic voltammetry.

Keywords: Azine electrolyte; electrocatalytic effect; ZnS loaded TiO₂; Glassy carbon electrode.

1. INTRODUCTION

Cyclic voltammetry (CV) is an electroanalytical technique of great importance. There are different oxidation states possible in inorganic compound metal centres. The CV establishes important information about the oxidation state of an element in a compound as well as the compound's stability under the experimental conditions employed. Electrochemical analyses have proved to be very responsive for the determination of organic molecules, drugs and related molecules in pharmaceutical dosage forms and biological fluids [1-5]. Glassy carbon electrode (GCE) have high impact in electrochemical analysis due to their low residual current, broad potential window, rich surface chemistry, low economic cost, low porosity and appropriateness for various sensing and detection applications [6]. Electron transfer rates that are seen at these electrodes are usually slower than on noble metal electrodes [7]. Chemically modified electrodes have received interest because of their improvement of the selectivity and sensitivity. Many kind methods have been proposed for surface modification of electrode, such as adsorption, covalent bonding and polymer covering [8]. The surface modification of working electrodes has been important development in electroanalysis. A plenty of efficient catalysts have been developed to escalate

the reduction or oxidation and enhance the cathodic peak current or anodic peak current of organic compounds [9, 10]. The variety of materials have been used in modification of GCE surface such as graphene [11], multi-walled carbon nanotubes [12], poly-4-nitroaniline [13], Polymeric Meso-Tetrakis(tetrabromo) Thiophenylporphyrin [14], Cu doped gold nanoparticles [15], palladium nanoparticles [16]. Azines are captivate compound for organic chemist because of their anti-leukemia activity [17], antitumor evaluation [18], intermediate in heterocyclic synthesis [19], undergoes crisscross cycloaddition reactions [20], NLO materials [21], pigments [22], dyes [23], organic semiconductor, blue-emitters, organic light-emitting diode [24], and organic photovoltaic application [25]. Herein, GC and Pt surface modified electrodes have been prepared by using ZnS loaded TiO₂ and bare TiO₂ materials. In this present study, surface modified electrodes are exhibiting enhanced electrochemical sensitivity for azines electrolyte. Finally we report electrocatalytic effect not only depends upon nature and porosity of electrode material, but also on nature of electrolyte.

2. EXPERIMENTAL

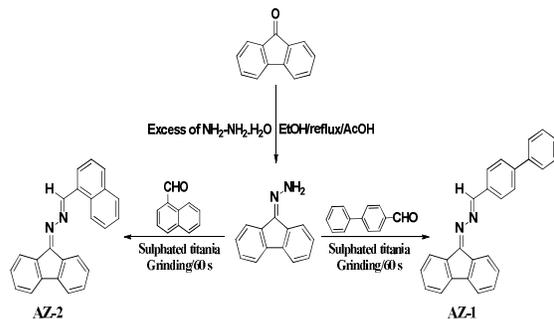
2.1. Synthesis of azines

2.1.1. Synthesis of (9H-fluoren-9-ylidene) hydrazine

About 0.01 M of fluorenone (1.8 g) dissolved in 50 ml of ethanol was refluxed with 0.1 M of hydrazine hydrate (5 ml) in the presence of acetic acid. The reaction mixture was allowed to cool over night. The solid thus formed was washed thoroughly with water to remove excess of unreacted hydrazine hydrate and impurities. It was recrystallized from absolute ethanol.

2.1.2. Synthesis of (E)-1-benzylidene-2-(9H-fluoren-9-ylidene) hydrazine (AZ-1)

Sulphated titania is prepared in literature [26]. To a mixture of fluorenone hydrazone (1 mmol) and biphenyl-4-carboxaldehyde (1 mmol) in dry media, 0.1 g of $\text{TiO}_2\text{-SO}_4^{2-}$ is added and the mixture is ground in a mortar with a pestle at room temperature for 60 seconds. The reaction is monitored by Thin Layer Chromatography (TLC). At the end of the reaction, ethyl acetate is added to the solidified mixture and the insoluble catalyst is separated by filtration. The solvent is evaporated to get the product. The crude sample is recrystallized from absolute ethanol. The above reaction is proposed in scheme 1. (E)-1-(9H-fluoren-9-ylidene)-2-(naphthalen-1-ylmethylene)hydrazine (AZ-2) synthesized in similar manner. AZ-1 and AZ-2 are characterized by FT-IR, ^1H and ^{13}C NMR spectral analysis.



Scheme - 1: Synthetic way of AZ-1 and AZ-2.

2.1.3. (E)-1-([1,1'-biphenyl]-4-ylmethylene)-2-(9H-fluoren-9-ylidene)hydrazine (AZ-1)

IR (KBr) (cm^{-1}): 1538 (C=N stretching), 3088 (Aromatic CH); ^1H NMR (CDCl_3 , 400 MHz) (δ , ppm): azomethine proton 8.61 (s, 1H), aromatic protons 7.29–8.50.

2.1.4. (E)-1-(9H-fluoren-9-ylidene)-2-(naphthalen-1-ylmethylene)hydrazine (AZ-2)

IR (KBr) (cm^{-1}): 1537 (C=N stretching), 3097 (Aromatic CH); ^1H NMR (CDCl_3 , 400 MHz) (δ , ppm): azomethine proton 9.27 (s, 1H), aromatic protons 7.26–8.93.

2.1.5. Preparation standard azine electrolyte solution

About 0.112 and 0.103 g of AZ-1 and AZ-2 are taken in 25 ml volumetric flasks and

dimethylformamide (DMF) is added up to mark of the flask and the solutions are sonicated for 15 min. 0.1 M tetrabutylammonium perchlorate (TBAP) solution is also prepared and it used as supporting electrolyte.

2.2. Preparation of electrodes

2.2.1. Preparation of ZnS loaded TiO_2

Precipitation cum sol-gel method was used to synthesis of ZnS loaded TiO_2 electrode material. A solution of Zinc nitrate (0.0891 g (0.03 M) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 5 mL of water) is added to solution of Na_2S (0.276 g (0.03 M) of Na_2S in 5 mL of water) and it resulted in formation of ZnS precipitate. The precipitate is added to a mixture of 12.5 mL of titanium isopropoxide and 80 mL of isopropanol under magnetic stirring at 60–70 °C (sol). This sol was stirred for 2 h, precipitate thus obtained is filtered, washed thoroughly with distilled water, dried at 100 °C in an air oven for 2 h and calcined at 400 °C for 12 h. ZnS loaded TiO_2 was formed as white powder [27].

2.2.2. Preparation of ZnS loaded TiO_2 modified glassy carbon electrode

GCE was polished to a mirror-like finish using a 1.0, 0.3 and 0.05 micron alumina powder on a polishing cloth. After polishing the GCE, it is allowed to sonicate for 10 min in 10% H_2SO_4 and then wiped with absolute ethanol and dried in air. About 2 mg of ZnS loaded TiO_2 is sonicated with ethanol for 15 min (casted). The casted ZnS loaded TiO_2 dipped on GC electrode surface is dried for 15 min in air. Nafion solution is placed in GC electrode surface with ZnS loaded TiO_2 and it is allowed to dry on air (GCNCZDTME). all modified electrodes are prepared according to the above mentioned procedure.

3. RESULT AND DISCUSSION

3.1. Scanning electron microscopy (SEM)

SEM measurements are performed to investigate the morphologies of bare glassy carbon electrode and its modified topology with TiO_2 and ZnS loaded TiO_2 was observed in SEM image with the accelerating voltage of 5 kV (Figure 1). Comparatively the morphology of glassy carbon surface changed due to binding of electrode materials (TiO_2 and ZnS loaded TiO_2).

3.2. Pros in azine synthesis

In preparation of unsymmetrical azines by normal (thermal) method, there are several disadvantages like high reaction time, low yield, using of baleful solvents and purification. Above mentioned defects cannot be seen when solid acid catalyst $\text{TiO}_2\text{-SO}_4^{2-}$ is employed. Scheme 2 represents formation of hydrazone to azine while using sulphated titania.

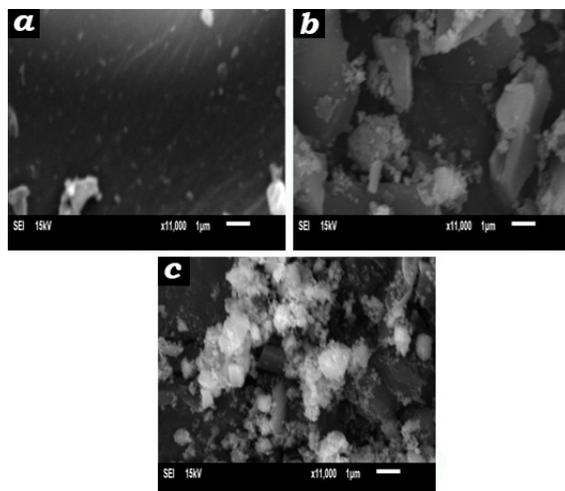
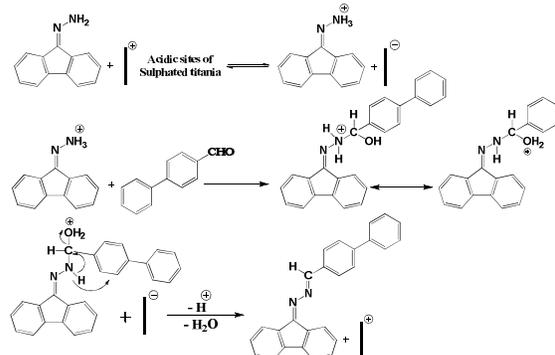


Figure - 1: SEM photographs of (a) bare glassy carbon electrode (b) GCNCTM electrode (c) GCNCZDTM electrode.



Scheme - 2: Mechanism of formation of AZ-1.

3.3. Electrochemical behavior of azines electrolyte at different working electrodes

Cyclic voltammetry is an ideal and valuable tool for monitoring electron transformation of modified electrode [28]. Electrochemical properties of 0.00125 M azines 15 and 16 are studied in dimethylformamide (DMF) by using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Cathodic peak potential and peak current was analyzed for different electrolyte (azines) in bare and modified electrodes scan between -2.0 to 2.0. Electrocatalytic effects of azines are examined with six electrodes (both bare and modified) in azine electrolyte. Table 1 and Figure 2 showcase the electrocatalytic effect of AZ-1 in GC, Pt and the modified electrodes with TiO₂ and ZnS loaded TiO₂ electrodes. For AZ-1 these are respective -E_{pc} (V) and -i_{pc} (e⁻⁵A) values observed with GCE (S1) (1.428, 3.385), GCNCTME (S2) (1.4368, 6.084), GCNCZDTME (S3) (1.3867, 9.803), PtE (S4) (1.4331, 1.792), PTNCTME (S5) (1.3488, 4.061), PTNCZDTME (S6) (1.4182, 3.605). In AZ-1, GCNCZDTME greatly improved cathodic peak

current is observed when compared with entire bare and modified electrodes. The reason for the better performance of the GCNCZDTME may be due to the electronic structure and the topological defects present on the GCNCZDTME surfaces. Analyzing the results, GCNCZDTME has exclusively improved the cathodic peak current compared to GCNCTME. PTNCTME has increased the cathodic peak current than the increase given by PTNCZDTME. If the electrocatalytic effect depends upon nature and porosity of the electrode materials, PTNCZDTME should have escalated the peak current, but the result has not been like that. Hence, it can be concluded that electrocatalytic effect not only depends upon nature and porosity of electrode material, but also on nature of electrolyte. The modified electrodes help for easy reduction for AZ-1. GC and their modified electrodes showcases the better catalytic performance of AZ-1 compared to Pt and its modified electrodes. This is because GC electrode has high density and low porosity and hence conducts ions faster. Same electrocatalytic effects are observed for AZ-2 (Table 2 and Fig. 3). GC, PtE and its modified electrodes have better catalytic activity on electrolyte in such a manner,

AZ-1: GCNCZDTME > GCNCTME > PTNCTME > PTNCZDTME > GCE > PtE

AZ-2: GCNCZDTME > GCNCTME > PTNCZDTME > GCE > PTNCTME > PtE

Higher and lower cathodic peak current was observed in AZ-1 while using GCNCZDTME and PtE.

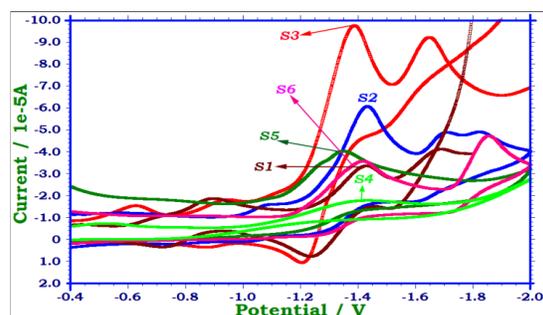


Figure - 2: Electrocatalytic effect of AZ-1 at GCE (S1) GCNCTME (S2) GCNCZDTME (S3) PtE (S4) PTNCTME (S5) PTNCZDTME (S6).

3.4. Loading effect on electrolyte

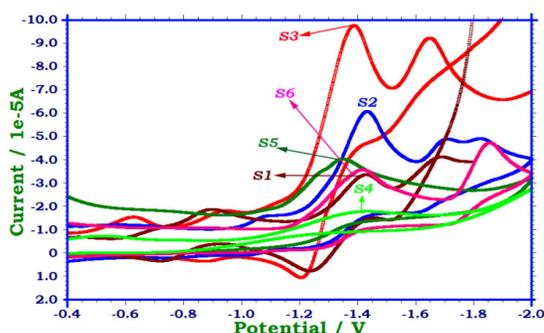
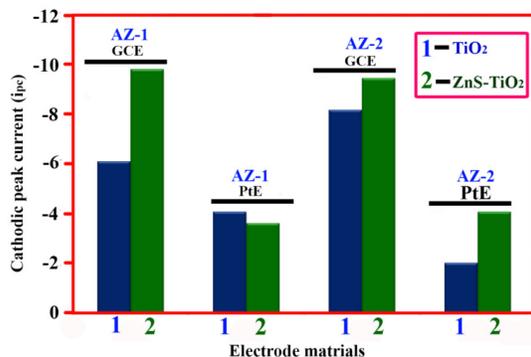
Figure 4 Showcase electrochemical sensitivity variation in azine electrolyte at bare TiO₂ and ZnS loaded TiO₂ modified electrodes. ZnS loaded TiO₂ modified glassy carbon and platinum electrodes are highly enhances cathodic peak current (i_{pc}) when compared bare titania modified electrodes. It concludes ZnS loaded TiO₂ modified electrodes are conducts the ions faster in azine electrolyte (Expect AZ-1 at PTNCTME).

Table - 1: Cathodic peak potential (E_{pc}) and peak current (i_{pc}) of AZ-1 at bare and modified working electrodes

Electrolyte	Scan rate (mV)	Working electrode	$-E_{pc}$ (V)	$-i_{pc}$ ($e^{-5}A$)
AZ-1	100	GCE (S1)	1.4280	3.385
		GCNCTME (S2)	1.4368	6.084
		GCNCZDTME (S3)	1.3867	9.803
		PtE (S4)	1.4331	1.792
		PTNCTME (S5)	1.3488	4.061
		PTNCZDTME (S6)	1.4182	3.605

Table - 2: Cathodic peak potential (E_{pc}) and peak current (i_{pc}) of AZ-2 at bare and modified working electrodes

Electrolyte	Scan rate (mV)	Working electrode	$-E_{pc}$ (V)	$-i_{pc}$ ($e^{-5}A$)
AZ-2	100	GCE (S1)	1.3333	3.803
		GCNCTME (S2)	1.3179	8.156
		GCNCZDTME (S3)	1.3488	9.444
		PtE (S4)	1.3488	1.946
		PTNCTME (S5)	1.3131	2.005
		PTNCZDTME (S6)	1.3539	4.064

**Figure - 3: Electrocatalytic effect of AZ-2 at GCE (S1) GCNCTME (S2) GCNCZDTME (S3) PtE (M4) PTNCTME (S5) PTNCZDTME (S6).****Figure - 4: Loading effect on electrolyte.**

4. CONCLUSION

Organic electrolytes (azines) are successfully synthesized by using sulphated

titania with solvent free and operational simplicity. GC and Pt electrode surfaces modified with bare titania and zinc sulfide loaded titania are used to examine electrocatalytic effect of azine electrolyte. The electrocatalytic performance will be more at GC modified electrodes than the Pt modified electrodes in AZ-1 and AZ-2 electrolyte. AZ-1 and AZ-2 has more catalytic activities in GCNCZDTME. This study highlights that electrocatalytic activity not only depends on nature, porosity and conductivity of electrode material but it also depends up on nature of electrolyte. The electrocatalytic performance will be more in GC modified electrodes then the Pt modified electrodes. Probably ZnS loaded TiO_2 modified electrodes (both GC and PtE) highly enhances cathodic peak current when compared bare TiO_2 modified electrodes.

5. REFERENCES

1. Uslu B and Ozkan SA. Electrochemical characterisation of nefazodone hydrochloride and voltammetric determination of the drug in pharmaceuticals and human serum. *Analytica Chimica Acta*. 2002; 462 (1): 49–57.
2. Kauffmann JM, Prete MP, Vire JC and Patriarche GJ. Voltammetry of pharmaceuticals using different types of modified electrodes. *Fresenius J. Anal. Chem.* 1985; 321(2): 172–176.
3. Belal F, Abdinic H and Zoman N. Voltammetric determination of nilvadipine in dosage forms

- and spiked human urine. **J. Pharm. Biomed. Anal.** 2001; 26 (4): 585–592.
- Zuman P. Current status of polarography and voltammetry in analytical chemistry. **Anal. Lett.** 2000; 33 (2): 163–174.
 - Demircigil TB, Ozkan SA, Coruh O and Yilmaz S. Electrochemical behaviour of formoterol fumarate and its determination in capsules for inhalation and human serum using differential pulse and square wave voltammetry. **Electroanalysis.** 2002; 14 (2): 122–127.
 - Uslu B and Ozkan SA. **Comb. Chem. High T. Scr.** 2007; 10: 495–513.
 - Canales C, Gidi L and Ramirez G. Electrochemical activity of modified glassy carbon electrodes with covalent bonds towards molecular oxygen reduction. **Int. J. Electrochem. Sci.** 2015; 10: 1684–1695.
 - Raj CR and Ohsaka TJ. **Electroanal. Chem.** 2001; 496: 44–49.
 - Damos FS, Sotomayor MDPT, Kubota LT, Tanaka SMCN and Tanaka AA. Iron (III) tetra-(N-methyl-4-pyridyl)-porphyrin as a biomimetic catalyst of horseradish peroxidase on the electrode surface: An amperometric sensor for phenolic compound determinations. **Analyst.** 2003; 128: 255–259.
 - Marzal PC, Torres KYC, Hoehr NF, Neto GO and Kubota LT. Determination of reduced glutathione using an amperometric carbon paste electrode chemically modified with TT-TCNQ. **Sens. Actuators.B.** 2004; 100: 333–340.
 - Raj MA and John SA. Graphene layer modified glassy carbon electrode for the determination of norepinephrine and theophylline in pharmaceutical formulations. **Anal. Methods.** 2014; 6: 2181–2188.
 - Raof JB, Ojani R, Baghayeri M and Aref MA. Application of a glassy carbon electrode modified with functionalized multi-walled carbon nanotubes as a sensor device for simultaneous determination of acetaminophen and tyramine. **Anal. Methods.** 2012; 4: 1579–1587.
 - Oztekin Y, Tok M, Nalvuran H, Kiyak S, Gover T, Yazicigil Z, Ramanaviciene A and Ramanavicius A. Electrochemical modification of glassy carbon electrode by poly-4-nitroaniline and its application for determination of copper(II). **Electrochimica Acta.** 2010; 56: 387–395.
 - Segura R, Velez J, Godoy F, Oyarzun MP, Sepulveda P and Aguirre MJ. Preparation of glassy carbon electrode modified with polymeric meso-tetrakis(tetrabromo thienyl)porphyrin for Determination of Cadmium and Lead by Anodic Stripping Voltammetry. **Int. J. Electrochem. Sci.** 2013; 8: 12005 – 12014.
 - Lin X, Ni Y and Kokot S. Electrochemical mechanism of eugenol at a Cu doped gold nanoparticles modified glassy carbon electrode and its analytical application in food samples. **Electrochim. Acta.** 2014; 133: 484–491.
 - Shi Q and Diao G. The electrocatalytic reduction of m-nitrophenol on palladium nanoparticles modified glassy carbon electrodes. **Electrochim. Acta.** 2011; 58: 399–405.
 - Sun CW, Wang HF, Zhu J, Yang DR, Xing J and Jin J. Novel symmetrical trans-bis-Schiff bases of N-substituted-4-piperidones: synthesis, characterization, and preliminary antileukemia activity measurements. **J. Heterocyclic Chem.** 2013; 50: 1374–1380.
 - Bondock S, Gieman H and Shafei A. Selective synthesis, structural studies and antitumor evaluation of some novel unsymmetrical 1-hetaryl-4-(2-chloroquinolin-3-yl)azines. **J. Saudi Chem. Soc.** 2015 (Article in press)
 - Zachova H, Man S, Taraba J and Potacek M. Rearrangement of fused tetracyclic heterocycles induced by alkyl halides and formation of a new type of 'proton sponge'. **Tetrahedron**, 2009; 65: 792–797.
 - Radl S. Crisscross cycloaddition reactions. **Aldrichim. Acta.** 1997; 30: 97–100.
 - Manas MM, Pleixats R, Andreu R, Garin J, Orduna J, Villacampa B, Levillain E and Salle M. The first 1,3-dithiol-2-ylidene donor- π -acceptor chromophores containing an azine spacer: synthesis, electrochemical and nonlinear optical properties. **J. Mater. Chem.** 2001; 11: 374–380.
 - Montagner C, Bacci M, Bracci S, Freeman R and Picollo M. Library of UV-Vis-NIR reflectance spectra of modern organic dyes from historic pattern-card coloured papers. **Spectrochim. Acta. A. Mol. Biomol. Spectrosc.** 2011; 79 (5): 1669–1680.
 - Vennerstrom JL, Makler MT, Angerhofer CK and Williams JA. Antimalarial dyes revisited: xanthenes, azines, oxazines, and thiazines. **Antimicrob. Agents. Chemother.** 1995; 39 (12): 2671–2677.

24. Glaser R, Knotts N, Yu P and Li L. Chandrasekhar M, Martin C, Barnes CL. Perfect polar stacking of parallel beloamphiphile layers. Synthesis, structure and solid-state optical properties of the unsymmetrical acetophenone azine DCA. **Dalton Trans.** 2006; 2891–2899.
25. Jedryka AJ, Bijak K, Sek D, Siwy M, Filapek M, Malecki G, Kula S, Lewinska G, Nowak EM, Sanetra J, Janeczek H, Smolarek K, Mackowski S and Balcerzak ES. Unsymmetrical and symmetrical azines toward application in organic photovoltaic. **Opt. Mater.** 2015; 39: 58–68.
26. Krishnakumar B and Swaminathan M. An expeditious and solvent free synthesis of azine derivatives using sulfated anatase–titania as a novel solid acid catalyst. **Catalysis Communications.** 2011; 16: 50–55.
27. Dhatshanamurthi P, Subash B, Senthilraja A, Kuzhalosai V, Krishnakumar B and Shanthi M. Synthesis and characterization of ZnS–TiO₂ photocatalyst and its excellent sun light driven catalytic activity. **Journal of Nanoscience and Nanotechnology.** 2013; 13: 1–10.
28. Xinga X, Liu S, Yua J, Liana W and Huang J. Electrochemical sensor based on molecularly imprinted film at polypyrrole-sulfonated graphene/hyaluronic acid-multiwalled carbon nanotubes modified electrode for determination of tryptamine. **Biosens. Bioelectron.** 2012; 31: 277–283.