Int. J. Electrochem. Sci., 10 **(2015)** 1384 - 1392

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Determination of 4-nitrophenol at Iron Phthalocyanine Decorated Graphene Nanosheets Film Modified Electrode

*Rajkumar Devasenathipathy, Veerappan Mani, Shen-Ming Chen**,
Kesavan Manibalan, Sheng-Tung Huang

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology,
No.1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan (R.O.C).
*E-mail: smchen78@ms15.hinet.net

Received: 18 October 2014 / *Accepted:* 6 November 2014 / *Published:* 16 December 2014

We described a sensitive electrochemical sensor for the determination of 4-nitro phenol (4-NP) at graphene nanosheets (GNS) decorated iron phthalocyanine (FePc) film modified electrode. GNS supported FePc composite was prepared by simple chemical reduction method and its formation was confirmed by scanning electron microscopy and energy-dispersive X-ray spectroscopy methods. GNS-FePc composite film modified glassy carbon electrode (GCE) has been prepared which exhibited excellent electrocatalytic ability towards electrochemical reduction of 4-NP in terms of less overpotential and enhanced peak currents. The influence of pH of the supporting electrolyte to the reduction of 4-NP has been investigated. Different scan rate studies has revealed that the reduction of 4-NP occurring at the GNS-FePc/GCE is diffusion controlled process. The GNS-FePc film modified GCE exhibited excellent electrocatalytic parameters such as wide linear range, high sensitivity and low detection limit. Practical feasibility of the sensor has been assessed in human urine samples. Moreover, the sensor has shown excellent stability, repeatability and reproducibility.

Keywords: Graphene, iron phthalocyanine, 4-nitrophenol, electrochemistry, electrocatalysis, cyclic voltammetry.

1. INTRODUCTION

4-nitrophenol (4-NP) is an important phenol based aromatic nitro compound widely used in the synthesis of pesticides, fungicides, industrial chemicals and pharmaceutical products [1-5]. It is non-degradable and highly soluble in aquatic environment. It has high persistent in environment, particularly in groundwater for long time [6, 7]. However, 4-NP is considered as anthropogenic toxicants and carcinogenic and hence it can severely damage the plants and organisms [8-10]. It is also recognized as a hazardous food chain pollutant due to its long time persistence in agricultural crops [2, 11]. Therefore, sensitive determination of 4-NP is of great importance [5, 12-18]. Electrochemical methods have significant advantages over other analytical methods attributed to their simplicity, sensitive, selectivity, short reaction time, portability and direct use in point-of-care assays [19-22]. However, electrochemical detection of 4-NP at bare electrodes is seriously suffers from high overpotential, interference issues and less sensitivity [3]. Therefore, chemically modified electrodes are widely used to avoid these issues aiming to the preparation of highly efficient electrochemical sensors for the determination of 4-NP [15, 23].

Iron phthalocyanine (FePc) is one of the important phthalocyanine containing iron atom at the center and consisting of 18 π electrons with conjugated planar structure [19, 24]. FePc has shown excellent electrocatalytic ability and hence it is widely used as electrocatalysts for various electrochemical reactions [25, 26]. However, FePc alone is unstable on the electrode surface and has very low electrical conductivity [27, 28]. Therefore, FePc requires a suitable conducting support to deliver its electrochemical properties. Graphene nanosheets (GNS) are highly versatile two dimensional conducting support material and possess excellent physicochemical properties such as large surface area, high porosity, biocompatibility, wide electrochemical window, excellent electronic and mechanical properties [29-33]. Graphene oxide (GO), an oxygenated derivative of GNS is the perfect precursor for the preparation of GNS based composites owing to its inexpensive production from graphite and easy processing in aqueous dispersions [4, 34-36].

The main objective of the present work is to develop a sensitive modified electrode for the determination of 4-NP based on GNS stabilized FePc. The GNS-FePc composite was prepared by simple solution based chemical reduction method. The preparation of the composite is involving simple and easily adoptable reduction method which does not requiring any surfactants. The developed electrochemical sensor exhibited excellent electrocatalytic parameters such as wide linear range, high sensitivity and low detection limit.

2. EXPERIMENTAL

2.1. Reagents and apparatus

Graphite (powder, <20 μm), iron (II) phthalocyanines (Dye content ~90 %), 4-nitrophenol and hydrazine monohydrate were purchased from sigma-Aldrich and used as received. All the other reagents were purchased from sigma-Aldrich and used without further purification. The supporting electrolyte used for the electrochemical studies was 0.1 M Phosphate buffer solution (PBS), prepared using NaH_2PO_4 and Na_2HPO_4, while the pH was adjusted to get the desired pH using either H_2SO_4 or NaOH. Tap water is collected in our laboratory and used for the real sample analysis.

The electrochemical measurements were carried out using CHI 611A electrochemical work station (CH Instruments, Inc. (U.S.A)) supplied by Anatech Company Ltd., Taiwan. Electrochemical studies were performed in a conventional three electrode cell using BAS GCE as a working electrode (area 0.071 cm^2), Ag/AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. Prior to each experiment, the electrolyte solutions were deoxygenated with pre-purified N_2 for 15 min unless otherwise specified. Scanning electron microscopy (SEM) studies were performed using Hitachi S-3000 H scanning electron microscope (SEMTech Solutions, USA). Energy-dispersive X-ray (EDX) spectra were recorded using HORIBA EMAX X-ACT, Sensor + 24 V=16 W, resolutions at 5.9 keV (Horiba Productx-act horiba, SN: 55267).

2.2. Preparation of GNS-FePc composite and fabrication of GCE/GNS-FePc

GNS-FePc composite has been prepared by solution based chemical reduction approach. First, graphite oxide was prepared from graphite by modified Hummers method [37] and then exfoliated to graphene oxide (GO) via ultrasonic agitation for 1 h. 10 ml of FePc dispersion (0.02 M) in DMF was added to the as prepared GO (1 mg mL^{-1}) (w/w 2:1) and the resulting mixture was stirred for 1 h. Hydrazine monohydrate (1 ml) was added to the mixture and refluxed at 157°C for 12 h. Finally, the reaction mixture was cooled, filtered, washed with copious amount of water and ethanol and dried at 60°C for overnight. The obtained GNS-FePc composite was redispersed in DMF (0.5 mg mL^{-1}).

GCE surface was polished with 0.05 µm alumina slurry using a Buehler polishing kit, then washed with water, ultrasonicated for 4 min and dried. 6 µL dispersion of GNS-FePc composite was drop casted on the cleaned GCE surface and dried at ambient conditions. The modified electrode was named as GCE/GNS-FePc and used for further electrochemical experiments. As a control, GCE/GNS and GCE/FePc were also prepared accordingly.

3. RESULTS AND DISCUSSIONS

3.1 Surface morphological characterization of MWCNT-FeTsPc composite

The SEM image of FePc has shown uniform arrangement of bar shaped particles in micrometer range sizes (Figure 1A). EDX spectrum of FePc (Figure 2A) has shown signals corresponding to the presence of carbon, nitrogen and iron with weight percentages of 57.42, 33.35 and 9.23% respectively.

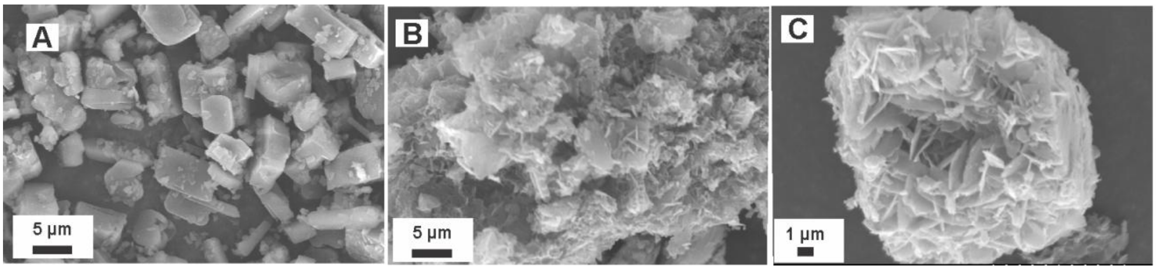


Figure 1. SEM images of FePc (A), GNS-FePc composite (B and C).

The SEM image of GNS-FePc composite presented uniform decoration of FePc at the surface of GNS sheets (Figure 1B and Figure 1C). Figure 1C clearly revealing that FePc bars were completely stabilized by GNS which shows that GNS can be a versatile support to prepare highly stable FePc. The

EDX spectrum of GNS-FePc composite (Figure 2B) is exhibited the signals corresponding to carbon, nitrogen, oxygen and iron with weight percentages of 49.96, 22.14, 18.18 and 9.72% respectively.

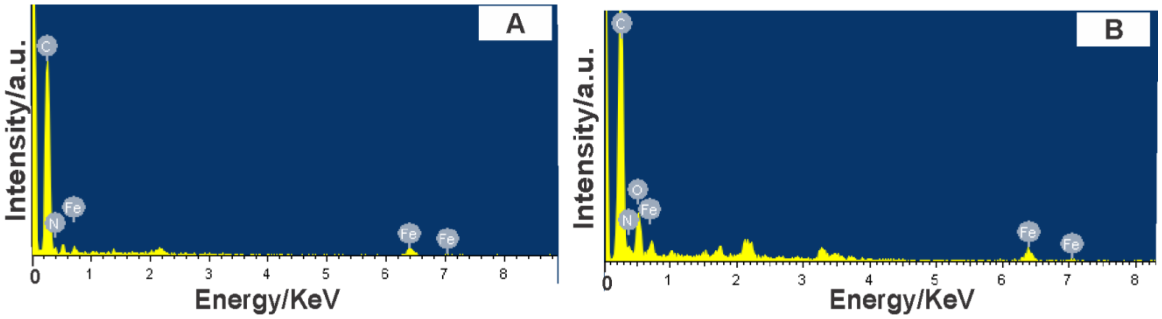
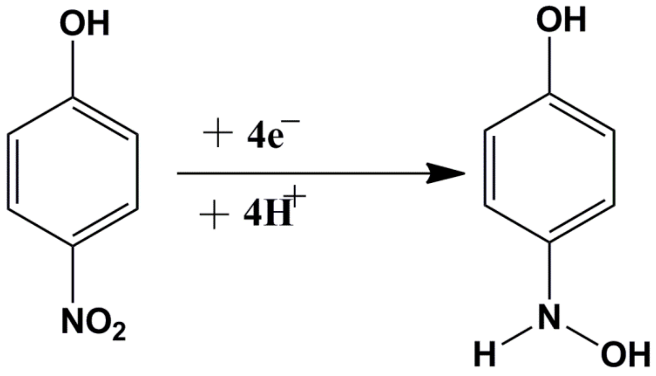


Figure 2. EDX spectrum of FePc (A) and GNS-FePc composite (B).

3.2 Electrocatalysis of 4-NP at GNS-FePc/GCE

Fig. 3 presents the CVs obtained at bare (a), FePc (b), GNS (c) and GNS-FePc (d) film modified GCEs in PBS (pH 7) containing 0.5 mM of 4-NP at the scan rate of 50 mV s^{-1}. The electrocatalytic behavior of these electrodes follows the order: bare GCE< FePc/GCE< GNS/GCE< GNS-FePc/GCE.



Scheme 1. The schematic representation for the reduction mechanism of 4-NP at GNS-FePc/GCE

Bare GCE does not exhibited any obvious reduction peak with quantifiable peak currents due to its poor electrocatalytic ability. FePc/GCE has exhibited a reduction peak at the potential of -0.85 V with small peak current. Despite the observation of reduction peak, FePc/GCE has shown high overpotential which may cause severe interferences. GNS/GCE and GNS-FePc/GCE are exhibited with highly enhanced and sharp peak currents at the potential of – 0.65 and – 0.75 V indicating their good electrocatalytic ability to the reduction of 4-NP. However, comparatively, GNS-FePc/GCE is exhibited maximum electrocatalytic performance than GNS/GCE in terms of less overpotential and high peak currents. Thus, GNS-FePc/GCE has shown excellent electrocatalytic ability to the reduction of 4-NP which must be attributed to the perfect synergy between large surface area and high conductivity of the GNS and good electrocatalytic ability of FePc. The mechanism for the reduction of 4-NP at GNS-FePc/GCE can be assigned from the literature as scheme 1, [3]

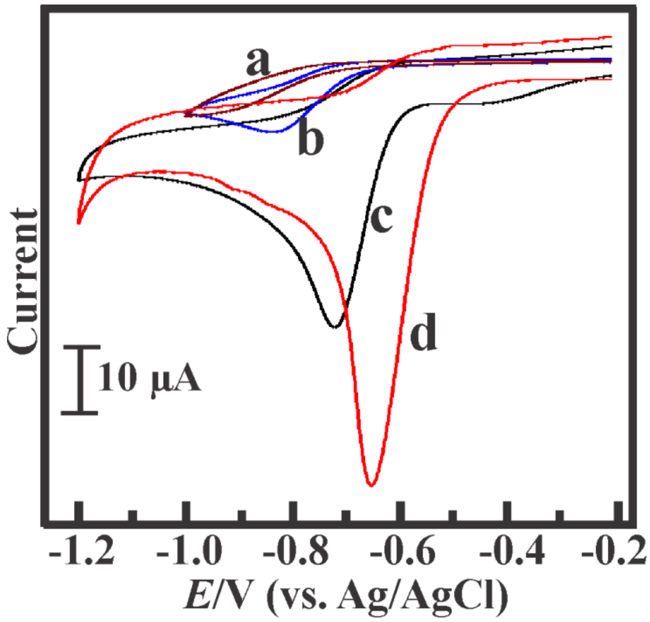


Figure 3. CVs obtained at bare (a), FePc (b), GNS (c) and GNS-FePc (d) film modified GCEs in PBS (pH 7) containing 0.5 mM of 4-NP. Scan rate = 50 mV s^{-1}.

3.3 Different pH studies

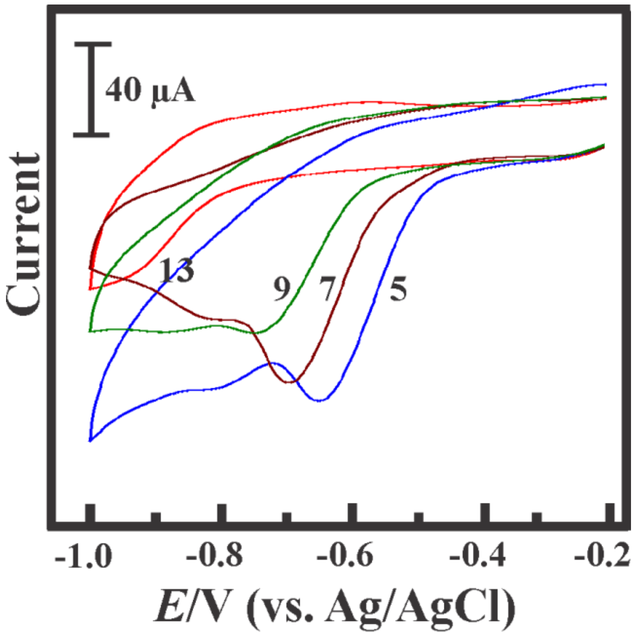


Figure 4. CVs obtained at GNS-FePc/GCE at different pH from 5–13 in PBS (pH 7) containing 0.1 mM 4-NP.

The effect of pH of the supporting electrolyte was investigated to understand the influence of various pHs towards reduction of 4-NP (Fig. 4). The electrocatalytic behavior of the GNS-FePc/GCE to the oxidation of 4-NP has been studied in PBS with different pH values (pH 5 to 13) containing 0.1 mM 4-NP (Fig. 4). As shown in the figure, the reduction peak of 4-NP has significantly influenced in various pH solutions. The peak current decreases with increasing pH from 5 to 13, while the peak potential varies drastically. The reduction peak current reaches maxima at acidic pH (pH 5), while it reach minimum at the basic pH (pH 13).

3.4 Different scan rates

The effect of scan rate (v) to the reduction of 4-NP (0.1 mM) was investigated in PBS (pH 7) at the scan rate ranges from 100 to 1000 mV s^{-1} (Fig. 5A). The reduction peak of 4-NP is increases with increase in the scan rates from 100 to 1000 mV s^{-1}. Moreover, the peak potentials of both the peaks were shifted to positive potentials upon scan rate increases. A plot between square root of scan rates ($v^{1/2}$) versus cathodic peak current has exhibited a linear relationship which indicating that the reduction process of 4-NP occuring at the GNS-FePc/GCE is a diffusion controlled electron transfer process (Fig. 5B).

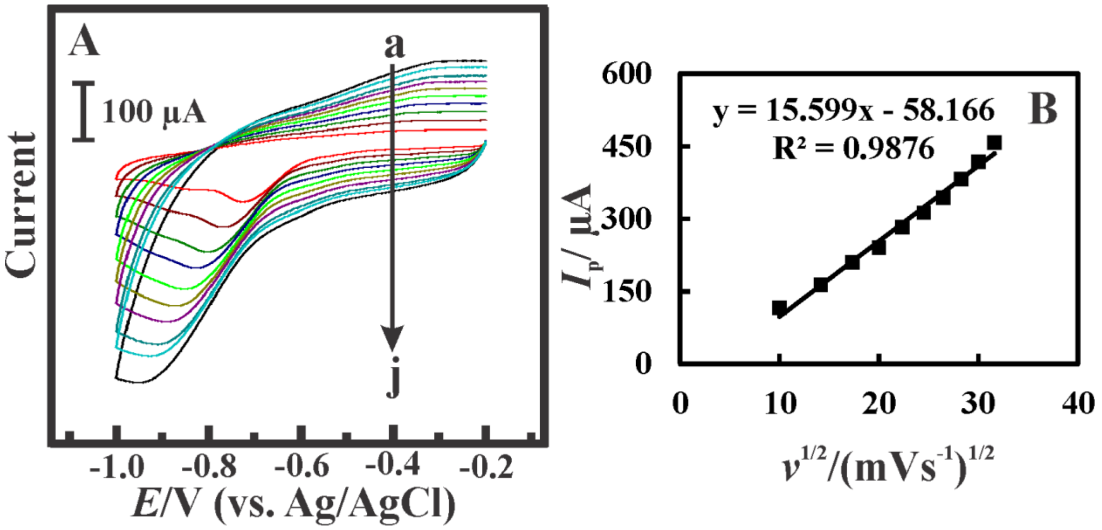


Figure 5. (A) CVs obtained at the GNS-FePc/GCE in PBS (pH 7) at different scan rates from 100 to 1000 Vs^{-1} in the presence of 0.1 mM 4-NP. (B) Plot of $v^{1/2}$ vs. I_p.

3.5 Determination of 4-NP

Fig. 6A shows the CVs obtained at GNS-FePc/GCE in PBS (pH 7) in the absence (curve a) and presence of 4-NP (curves b to h; each addition of 100 μM). The scan rate was hold at 50 mV s^{-1}. The reduction peak current attributed to the reduction of 4-NP has significantly increased upon addition of 100 μM concentration of 4-NP. The reduction peak current is increases upon further additions of 4-NP.

The linear increase in the reduction peak currents has shown the efficient electrocatalytic ability of the GNS-FePc/GCE. The GNS-FePc/GCE based sensor exhibited quick and sensitive responses for the each addition of 4-NP. A calibration plot was made between the concentration of 4-NP versus response current (Fig. 6B) and the respective linear regression equation can be expressed as I_p (µA) = 0.1193 [4-NP] (µA/µM) + 8.122. The response current for the each addition of 4-NP was increases linearly over the wide linear range between 100 µM and 0.7 mM. The sensitivity of the sensor has been estimated to be 1.68 µA µM^{-1} cm^2, while the limit of detection (LOD) was calculated to be 10 µM. The sensor exhibited quite comparable performance with other sensors in terms of wide linear range, low detection limit and high sensitivity [2, 3].

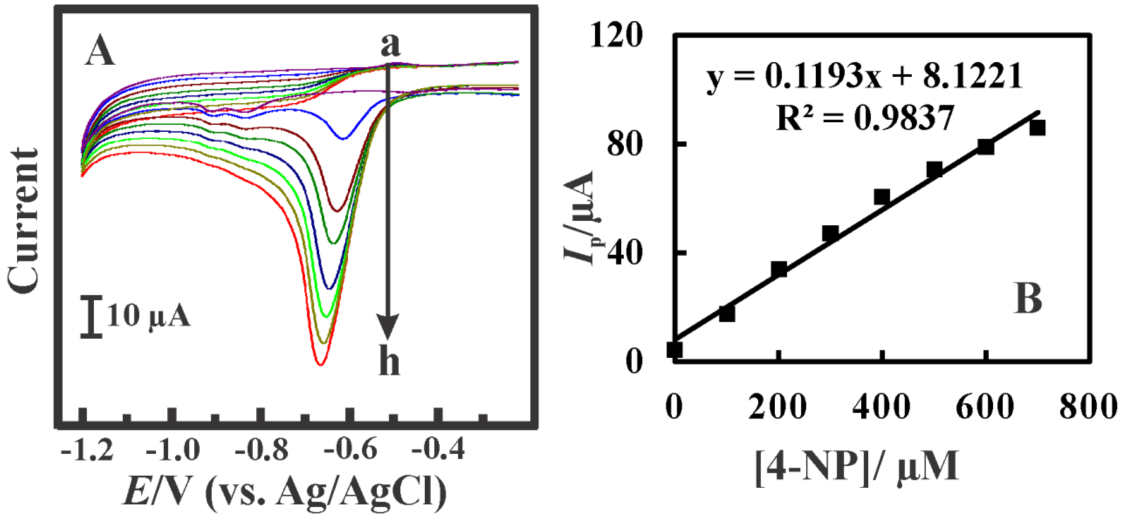


Figure 6. (A) CVs obtained at GNS-FePc/GCE in PBS (pH 7) in the absence (a) and presence of each addition of 100 µM 4-NP (curves b to h) at the scan rate of 50 mVs^{-1}. (B) Plot shows I_p vs. [4-NP]

3.6 Determination of 4-NP in real samples

Practicality of the GNS-FePc/GCE was demonstrated in tap water samples. The experimental conditions are similar to the lab sample analysis. The spiked 4-NP concentrations were of 100 and 200 µM (Table 1). The obtained found and recovery results are acceptable and hence the sensor can be used for the determination of 4-NP present in real samples.

Table 1. Determination of 4-NP at GNS-FePc/GCE in water samples

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
1	100	98.76	98.76	2.1
2	200	198.5	99.25	2.7

3.7 Repeatability, reproducibility and stability studies

Repeatability and reproducibility of the GNS-FePc/GCE have been assessed in PBS (pH 7) containing 0.1 mM 4-NP. The sensor has exhibited appreciable repeatability with relative standard deviation (R.S.D) of 2.58 % for five repeatitive measurements carried out in single modified electrode. The sensor has shown acceptable reproducibility of 2.14% for five independent measurments carried out in six different electrodes.. During one month stroge period, the sensor was exhibited well defined electrocatalytic response towards reduciton of 4-NP. 96.23% of the initial catalytic response current was retained over one month of its continuous use revealing the excellent storage stability of the sensor.

4. CONCLUSIONS

In summary, we successfully prepared GNS-FePc/GCE through simple solution based chemical reduction method and employed it for the electrochemical determination of 4-NP. The successful formation of the GNS-FePc composite has been confirmed by SEM and EDX analysis. The GNS-FePc/GCE has exhibited excellent electrocatalytic abilty to the reduciton of 4-NP in terms of less ovrepotential and enhanced peak currents. The GNS-FePc/GCE sensor has exhibited excellent analytical parameters for the determination of 4-NP such as wide linear range from 100 μM to 0.7 mM, low LOD 10 μM and high sensitivity (1.68 $\mu A \mu M^{-1}$ cm^2). The practical feasibility of the sensor has been assessed in water samples. Also, the sensor offered appreciable stability, repeatability and reproducibility results.

ACKNOWLEDGEMENT
This work was supported by the National Science Council and the Ministry of Education of Taiwan (Republic of China).

References

1. P. Canizares, C. Sáez, J. Lobato, M. Rodrigo, *Ind. Eng. Chem. Res.,* 43 (2004) 1944.
2. R. Madhu, C. Karuppiah, S.-M. Chen, P. Veerakumar, S.-B. Liu, *Anal. Methods*, 6 (2014) 5274.
3. Y.-L. Yang, B. Unnikrishnan, S.-M. Chen, *Int.J. Electrochem. Sci.,* 6 (2011) 3902.
4. J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu, M. Liu, *J. hazard. Mater.,* 201 (2012) 250.
5. S. Hu, C. Xu, G. Wang, D. Cui, *Talanta*, 54 (2001) 115.
6. J. Das, M.A. Aziz, H. Yang, *J. Am. Chem. Soc.*, 128 (2006) 16022.
7. K. Esumi, R. Isono, T. Yoshimura, *Langmuir*, 20 (2004) 237.
8. J.A. Brecken-Folse, F.L. Mayer, L.E. Pedigo, L.L. Marking, *Environ. Toxicol. Chem.,* 13 (1994) 67.
9. M. Trapido, J. Kallas, *Environ. Technol.*, 21 (2000) 799.
10. G.E. Howe, L.L. Marking, T.D. Bills, J.J. Rach, F.L. Mayer, *Environ. Toxicol. Chem.,* 13 (1994) 51.

11. M. Koizumi, Y. Yamamoto, Y. Ito, M. Takano, T. Enami, E. Kamata, R. Hasegawa, *Toxicol. Sci.*, 26 (2001) 299.
12. K. Kuroda, T. Ishida, M. Haruta, *J. Mol. Catal. A: Chem.*, 298 (2009) 7.
13. V.d.A. Pedrosa, L. Codognoto, L.A. Avaca, *J. Brazil. Chem. Soc.*, 14 (2003) 530.
14. R. de Cássia Silva Luz, F.S. Damos, A.B. de Oliveira, J. Beck, L.T. Kubota, *Talanta*, 64 (2004) 935.
15. H. Yin, Q. Ma, Y. Zhou, S. Ai, L. Zhu, *Electrochim. Acta*, 55 (2010) 7102.
16. Y. Fan, J.-H. Liu, C.-P. Yang, M. Yu, P. Liu, *Sens. Actuators, B*, 157 (2011) 669.
17. A. Arvinte, M. Mahosenaho, M. Pinteala, A.-M. Sesay, V. Virtanen, *Microchim. Acta*, 174 (2011) 337.
18. H. SonáBae, K. HyunáPark, *J. Mater. Chem.*, 21 (2011) 15431.
19. V. Mani, A.E. Vilian, S.-M. Chen, *Int. J. Electrochem. Sci*, 7 (2012) 12774.
20. V. Mani, A.P. Periasamy, S.-M. Chen, *Electrochem. Commun.*, 17 (2012) 75.
21. R. Devasenathipathy, V. Mani, S.-M. Chen, *Talanta*, 124 (2014) 43.
22. R. Devasenathipathy, V. Mani, S.-M. Chen, D. Arulraj, V. Vasantha, *Electrochim. Acta*, 135 (2014) 260.
23. P. Zhang, C. Shao, Z. Zhang, M. Zhang, J. Mu, Z. Guo, Y. Liu, *Nanoscale*, 3 (2011) 3357.
24. A. Lever, J. Wilshire, *Inorg. Chem.*, 17 (1978) 1145.
25. V. Mani, R. Devasenathipathy, S.-M. Chen, J.-A. Gu, S.-T. Huang, *Renewable Energy*, 74 (2015) 867-874.
26. M. Alvaro, E. Carbonell, M. Esplá, H. Garcia, *Appl. Catal. B*, 57 (2005) 37.
27. J.H. Zagal, S. Griveau, J. Silva, T. Nyokong, F. Bedioui, *Coord. Chem. Rev.*, 254 (2010) 2755.
28. M.-S. Liao, S. Scheiner, *J. Chem. Phy.*, 114 (2001) 9780.
29. A.K. Geim, K.S. Novoselov, *Nat. Mater.*, 6 (2007) 183.
30. K. Novoselov, A.K. Geim, S. Morozov, D. Jiang, M.K.I. Grigorieva, S. Dubonos, A. Firsov, *Nature*, 438 (2005) 197.
31. V. Mani, B. Devadas, S.-M. Chen, *Biosens. Bioelectron.*, 41 (2013) 309.
32. B. Devadas, V. Mani, S.-M. Chen, *Int. J. Electrochem. Sci.*, 7 (2012) 8064.
33. V. Mani, S.-M. Chen, B.-S. Lou, *Int. J. Electrochem. Sci.*, 8 (2013) 11641.
34. Y. Liu, D. Yu, C. Zeng, Z. Miao, L. Dai, *Langmuir*, 26 (2010) 6158.
35. D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, *Chem. Soc. Rev.*, 39 (2010) 228.
36. J.-H. Yang, Y. Gao, W. Zhang, P. Tang, J. Tan, A.-H. Lu, D. Ma, *J. Phy. Chem.* C, 117 (2013) 3785.
37. W.S. Hummers Jr, R.E. Offeman, *J. Am. Chem. Soc.*, 80 (1958) 1339.