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Full Paper

Electrochemical Studies of Dopamine at Lithium Zirconate/SDS Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Abstract- Li_2ZrO_3 nanoparticles were synthesized by the Gel Combustion Process. The synthesized nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The synthesized Li_2ZrO_3 nanoparticles were used for the modification of carbon paste electrode and sodium docylsulphate (SDS) anionic surfactant was further modified by the immobilization technique for the electrochemical determination for dopamine at pH 7.2 phosphate buffer solution. The modified carbon paste electrode SDS/ Li_2ZrO_3 shows excellent electrochemical sensor for dopamine and also in the simultaneous determination dopamine, ascorbic acid and uric acid. The modified electrode showed high sensitivity, high reproducibility, easy preparation and regeneration of the electrode surface.

Keywords- Dopamine, Lithium Zirconate, Modified Carbon Paste Electrode, Electrocatalytic Oxidation, Sodium Docylsulphate (SDS), Cyclic Voltammetry

1. INTRODUCTION

In 1998, lithium zirconate(Li_2ZrO_3) was proposed by Nkagawa et al. [1,2] In recent years, Li_2ZrO_3 ceramics have been extensively studied for their applications as electronic devices in batteries and breeder materials for nuclear fusion reactors. [3,4] Li_2,ZrO_3, is a well-known material in the nuclear industry because of its properties, including high-tritium release rate, thermal stability, low thermal expansion, and properties, such as good compatibility with structural materials [5,6]. Generally Li-containing materials, such as lithium zirconate ($Li_2 ZrO_3$), have been reported to be promising candidates for CO_2 capture at high temperatures due to their merits such as high CO_2 capture capacity and stability, especially in the presence of steam, and easy regeneration [7].

Dopamine (DA) occurs in the central nervous system naturally in the basal ganglia where its function as a neurotransmitter as well as in the adrenal medulla. DA also known as 4-(2-aminoethyle) bengene -1,2–diol belongs to a member of the catecholamine family. Dopamine (DA) was discovered to be an important neurotransmitter in the mammalian central nervous system in the late 1950 and it is found in high amount (50 nmol/g) in a region of the brain known as "caudate nucleus" [8,9]. It is one of the excitatory neurotransmitters that play an important role in several physiological events. It is involved in the functioning of renal, cardiovascular, hormonal and nervous systems. DA is also involved in neurological diseases such as Parkinson's disease [10,11], Alzheimer's disease [12] and Schizophrenia disease [13]. It has been also suggested that DA plays a role in drug addiction [14] and some manifestation of HIV [15]. The fact that DA and other catecholamines are easily oxidizable compounds makes their detect ion possible by electrochemical methods based on anodic oxidation. Dopamine has been determined using various electrochemical methods [16].

Ascorbic acid (AA) is essential in human body due to its importance as an antioxidant. It is widely known as vitamin C, a water-soluble vitamin that is commonly required for metabolism and consumed on a large scale. Studies on the catalytic oxidation of ascorbic acid have been extensively conducted [17,18] Similarly, (AA) has been used for the prevention and treatment of the common cold, mental illness, infertility, and even cancer and AIDS [19,20]. Uric acid (UA) is the primary end product of purine metabolism in the human body [21]. In a healthy human being, the typical concentration of UA in urine is around 2 mM and in the blood is in between 120 μM to 450 μM ranges [22]. Extreme abnormalities of UA levels are symptomic of several diseases, such as, cardiovascular disease [23], hyperuricaemia, uric acid stones, gout and Leseh-Nyhan syndrome [24]. Recently, electrochemical sensors have attracted much attention due to their advantages of simplicity, cheapness, fast analysis along with high sensitivity and selectivity [25].

Surfactants, due to their favorable physicochemical properties are extensively used in many fields of technology and research, i.e. in pharmacy, in cosmetics, textile industry, agriculture, biotechnology [26]. Normally surfactant is a linear molecule with a hydrophilic

(attracted to water) head and a hydrophobic (repelled by water) end. Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode solution interface [27] and also improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants [28].

As part of our research work on the development of new electrochemical sensors for the determination of DA [29,30]. This work reports for the voltammetric behavior of DA at bare and Li_2ZrO_3 /SDS nanoparticle modified electrode showed an electrocatalytic activity for the oxidation of DA, AA and UA. The results indicate that the modified electrode could be used to detect DA in the presence of AA and UA effectively.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Lithium nitrate (98%, sd fine chemicals) and zirconylnitrate was purchased from Lobo chemicals were used as lithium and zirconia precursor respectively. Glycine was used as fuel. Lithium nitrate, zirconyl nitrate and glycogen were dissolved in double distilled water. Dopamine (DA) were obtained from Himedia chemical company and of analytical grade used without further purification. 25 mM DA stock solution was prepared in 0.1 M perchloric acid, AA and UA was prepared in double-distilled water. Graphite powder of 50 mm size was purchased from Loba and silicon oil was purchased from Himedia. The chemicals for preparation of buffer solution were purchased from Merck. Phosphate buffer (0.2 M pH 7.2) was used as supporting electrolyte.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire as counter electrode and saturated calomel as reference electrode.

2.3. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.4. Preparation of SDS/Li_2ZrO_3nanoparticle modified carbon paste electrode

SDS solution (10 µL) was added to the surface of the MCPE prepared from Li_2ZrO_3 nanoparticles for 5 min. The electrode was later thoroughly rinsed with water to removed unabsorbed modifier and dried in air at room temperature. The same procedure was followed for the preparation of the BCPE.

2.5. Synthesis of Li_2ZrO_3

Synthesis of Li_2ZrO_3 was carried out by the gel combustion process. Lithium nitrate (98%, sd fine chemicals) and zirconylnitrate (Lobo chemicals) were used as lithium and zirconia precursor respectively. Glycine was used as fuel and carefully weighed lithium nitrate, zirconyl nitrate and glycine were dissolved in 125 ml distilled water. Fuel to nitrate ratio (moleratio) was maintained as 0.35 in the reaction mixture. The beaker containing reaction mixturewas placed on a hot plate, and then heat was supplied to the beaker. Nitrates were released during the heating, resulted in gel formation. The reaction was completed by self-ignition combustion leaving behind fine white powder. The formed metal oxide was then calcinated at 500 °C and characterized by SEM and XRD. [31,32]

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of $K_4Fe(CN)_6$ at Li_2ZrO_3 /SDS nanoparticle MCPE

Fig. 1A shows the electrochemical response of Li_2ZrO_3 /SDS nanoparticle MCPE was studied by standard 1mM [$K_4Fe(CN)_6$] in 1 M KCl as a supporting electrolyte with scan rate 50 mV s^{-1} by CV technique.

At bare carbon paste electrode the voltammetric response of [$K_4Fe(CN)_6$] shows low current single owing to the complex properties and the roughness of the electrode surface (solid line). However in Li_2ZrO_3/SDS nanoparticle MCPE shows excellent enhancement peak current both in cathodic and anodic peak currents with SDS on the surface of electrode (dotted line). SDS is the anionic surfactant, on the surface of electrode which may alter the overvoltage of electrode and influence the rate of electron transfer.

3.2. Electrochemical response of $K_4Fe(CN)_6$ at Li_2ZrO_3nanoparticle MCPE

At bare carbon paste electrode, the cyclic voltammogram of $K_4Fe(CN)_6$ shows the less sensitive current signals (solid line) and in presence of 4 mg of lithium zirconate decreases the current signals (dotted line). This shows as such lithium zirconate is responsible for the decreases the current signals as shown in Fig. 1B. From the fig it is clear that lithium zirconate with SDS is good for the increase in current signals but only in presence of lithium zirconate doesn't show significant currents as compared to Li_2ZrO_3 /SDS modified electrode.

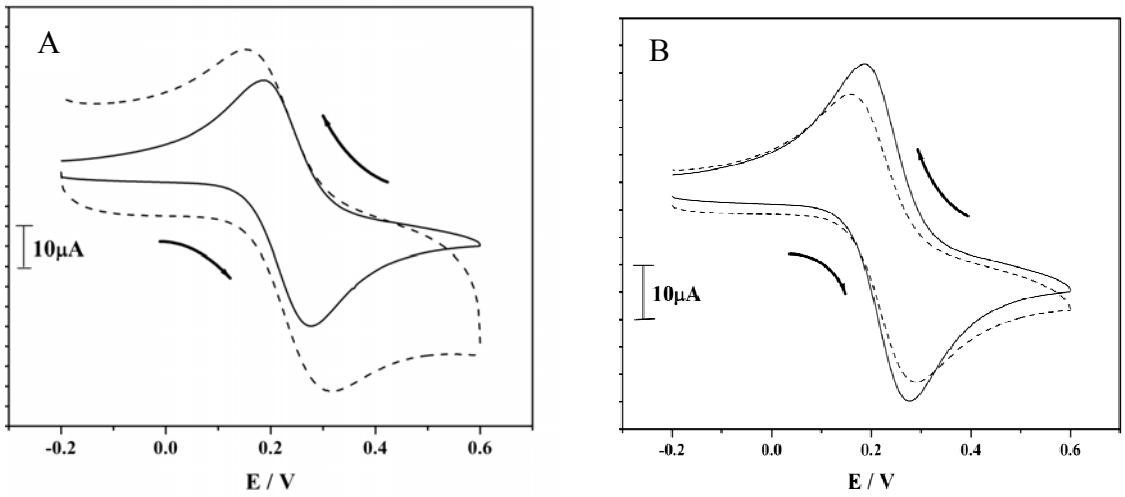

Fig. 1. A) Cyclic voltammogram of 1 mM $[K_4Fe(CN)_6]$ at BCPE (solid line) and SDS/ Li_2ZrO nanoparticle MCPE (dotted line) in 1 M KCl scan rate 50 mV s^{-1} B) Cyclic voltammogram of 1 mM $[K_4Fe(CN)_6]$ at BCPE (solid line) and Li_2ZrO_3 nanoparticle MCPE (dotted line) in 1 M KCl scan rate 50 mV s^{-1}

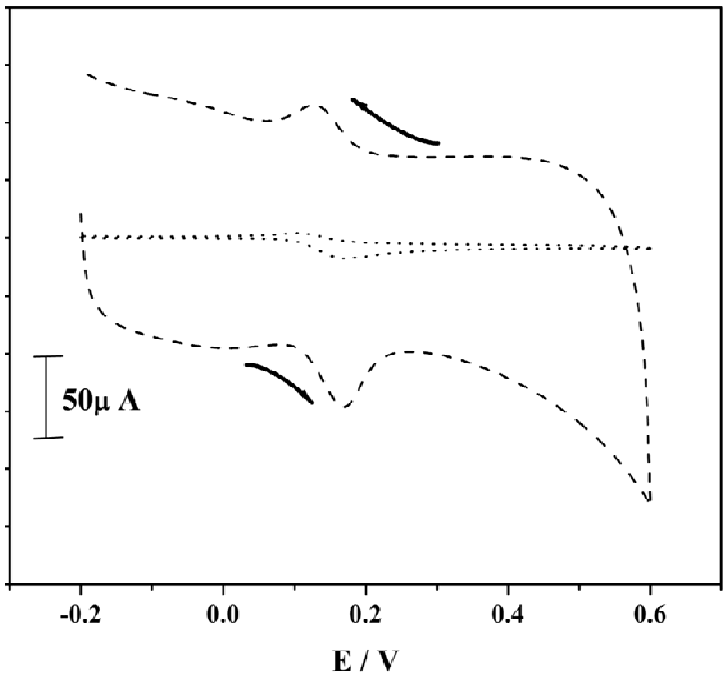

Fig. 2. Cyclic voltmmogram in 0.2 M phosphate buffer solution pH 7.2 at BCPE (dotted line) and SDS/Li_2ZrO_3 nanoparticle MCPE (dashed line) of 0.1×10^{-4} DA with scan rate of 50 mV s^{-1}

3. 3. Electrochemical response of DA at Li_2ZrO_3 /SDS nanoparticle MCPE

Dopamine is being an easily oxidisable catecholamine its voltammogramm was recorded in the potential range of -0.2 to 0.6 V *vs*. SCE in the 0.2 M phosphate buffer at pH 7.2 at 50 mV s^{-1}.

In Fig. 2 cyclic voltammogramms for BCPE (dotted line) shows low redox peak currents with high peak potential difference [ΔE_p=0.067 V] is compared to Li_2ZrO_3 /SDS nanoparticle MCPE shows high redox peak currents with minimization of over peak potential difference [ΔE_p=0.059 V] shows that the modified electrode acts as the electrocatalytic property in Li_2ZrO_3 /SDS MCPE is good for the detection of DA.

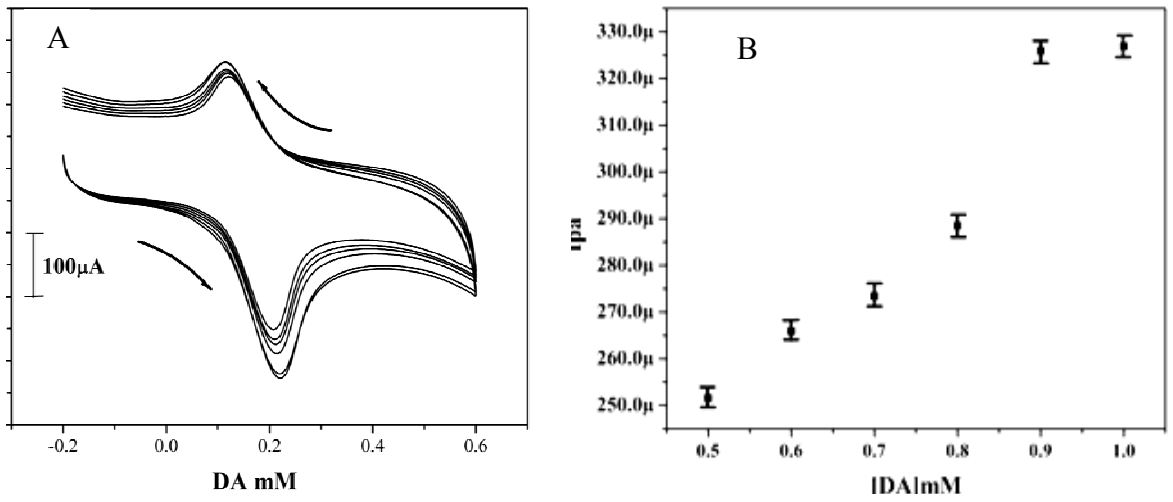

Fig. 3. A) Cyclic voltammogram of DA at different concentration at SDS/ Li_2ZrO_3 nanoparticle MCPE in 0.2 M PBS of pH 7.2 B) Graph of current V s^{-1} concentration of DA at scan rate 50 mV s^{-1} of pH 7.2

3. 4. Effect of concentration of DA

Electrocatalytic oxidation of DA was carried out by varying concentration at Li_2ZrO_3 /SDS nanoparticle MCPE from 0.5 mM to 1 mM shows in the Fig. 3A. By increasing the concentration of DA,both Ipa and I_{pc} goes on increasing with negligible shifting E_{pa} and E_{pc}. Fig. 3B shows I_{pa} *vs.* DA concentration that anodic peak current goes on increasing with increasing the DA concentration resulting the electrode processes is diffusion controlled [33-37].

3.5. Effect of concentration of SDS at Li_2ZrO_3 nanoparticle MCPE

Li_2ZrO_3 nanoparticle MCPE was further modified by SDS surfactant from the range 5 µl to 25 µl. The Fig. 4A shows the voltammetric response of SDS concentration at Li_2ZrO_3 nanoparticle MCPE with 0.1 mM DA at pH 7.2. By increasing the concentration of SDS (E_{pa}) oxidation peak potential shifts positive side and (E_{pc}) reduction peak potential shifts negative side. The Fig. 4B shows Ipa V s^{-1} SDS concentration the anodic peak current goes on increasing with increasing the concentration of SDS. In 20 µl shows high sensitivity in the presence of 0.1 mM DA after there is decrease in the current this is due to SDS surfactant molecule diffuses in the Li_2ZrO_3 nanoparticle MCPE and from a manolayer on the surface of the electrode and subsequently electrostatic interaction between adsorbed substrate and shows hydrophobic character in Li_2ZrO_3/SDS nanoparticle MCPE. This result shows that the method of modification shows maximum increases in the current signals.

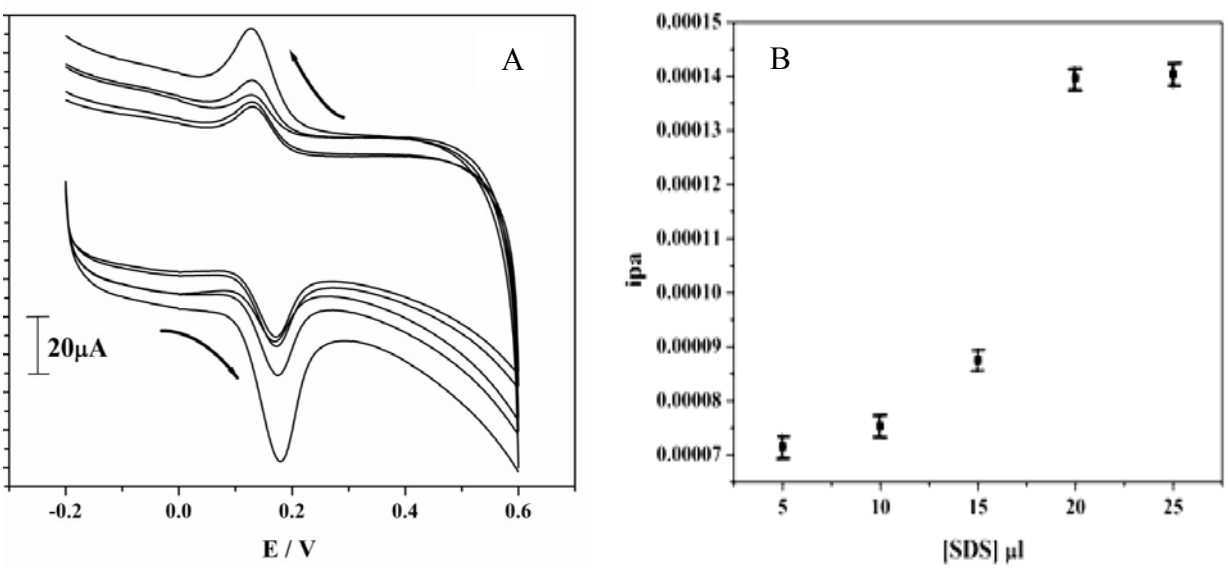

Fig. 4. A) Cyclic voltammogram of SDS at different concentration at SDS/ Li_2ZrO_3 nanoparticle MCPE in 0.2 M PBS of pH 7.2 B) Graph of current V s^{-1} concentration of SDS at scan rate 50 mV s^{-1} of pH 7.2

3.6. Electrocatalytic response of DA and AA at Li_2ZrO_3 /SDS nanoparticle MCPE

It is well known that ascorbic acid (AA) widely coexists with DA in real biological matrices. Therefore avoiding AA interference is an important target for any DA analytical methods. In Fig. 5, the voltammetric response of DA and AA at Li_2ZrO_3 /SDS nanoparticle MCPE at pH 7.2 with scan rate 50 mV s^{-1}. Li_2ZrO_3 /SDS nanoparticle MCPE DA exhibited enhanced peak currents in the presence of AA. The two well oxidation peaks and one reduction peak (solid line) separated between DA and AA. The electrocatalytic anodic peak

of DA was obtained at 197 mV and AA was found to be at 50 mV. This result shows that Li_2ZrO_3 /SDS nanoparticle MCPE acts as good sensor for the detection of DA in the presence of AA.

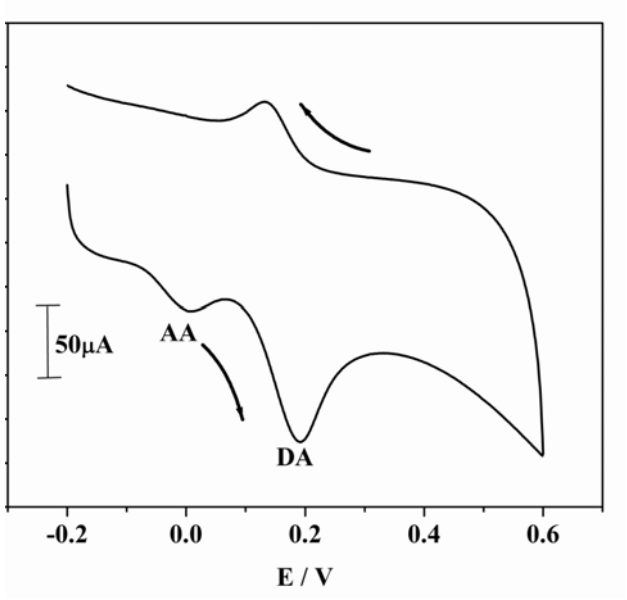

Fig. 5. Cyclic voltammogram obtained for oxidation of AA and DA at SDS/Li_2ZrO_3 nanoparticle MCPE (solid line) at scan rate of 50 mV s^{-1}, 0.2 M PBS (pH 7.2)

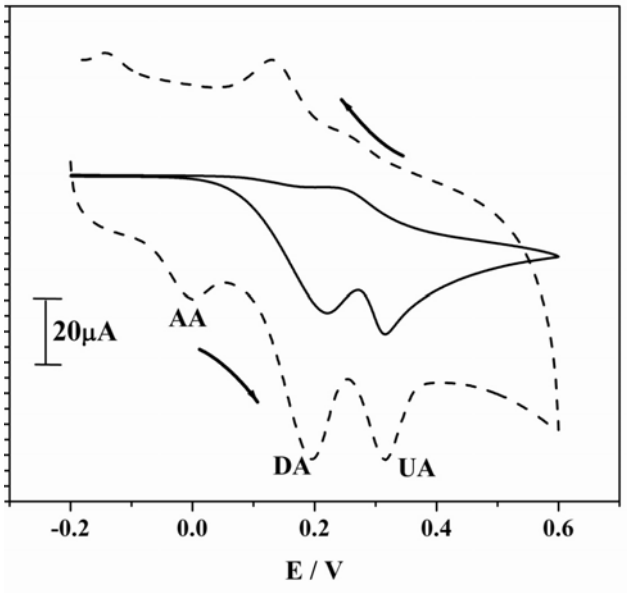

Fig. 6. Cyclic voltammogram obtained for obtained for the oxidation of AA, UA and DA at SDS/Li_2ZrO_3 nanoparticle MCPE (solid line) at bare (dotted line) at scan rate of 50 mV s^{-1}, 0.2 M PBS (pH 7.2)

3.7. Voltammetric simultaneous study of DA, AA and UA at Li_2ZrO_3 /SDS nanoparticle MCPE

In Fig. 6 shows the voltammograms for solution contains mixture of 1 mM AA, 0.1 mM DA and 0.5 mM UA in phosphate buffer at pH 7.2 in 50 mV s^{-1}. In bare (solid line) showed two oxidation peak and one reduction peak with low current signal currents. However in Li_2ZrO_3/SDS nanoparticle MCPE was able to separate the oxidation peaks of AA, DA and DA by showing three well oxidation peak and one reduction with high enhancement (solid line) .The separation peak of DA-UA was 0.190 V and DA-AA was 0.140 V obtained .The AA, DA and UA shows well oxidation peak individually. Hence Li_2ZrO_3 /SDS nanoparticle MCPE acts as a good sensor in the simultaneous study of neurotransmitter.

4. CONCLUSION

The bare carbon paste electrode was modified with Li_2ZrO_3 nanoparticle shows small decrease in current but in presence of SDS modified with Li_2ZrO_3 shows very good electrocatalyic property for the determination of dopamine. The modified electrode shows simultaneous determination of DA, AA and UA and the proposed method can be applied for the determination of bioactive molecule and this modified electrode acts as sensor for some neurotransmitters.

REFERENCES

[1] K. Nakagawa, and T. A. Ohashi, J. Electrochem. Soc. 145 (1998) 1344.
[2] R. H. Radfarnia, and M. C. Iliuta, Eng. Chem. Res. 50 (2011) 9295.
[3] L. Guo, X. Wang, S. Zhang, and C. Zhong, J. Mater. Sci. 46 (2011) 6960.
[4] T. Kinjyo, M. Nishikawa, M. Enoeda, and S. Fukada, Fus. Eng. Des. 83 (2008) 580.
[5] H. Kwast, E. H. P. Cordfunke, and R. P. Muis, "Fabrication, Properties, and Tritium Release Rates of Lithium Zirconates" in Ceramic Transactions, Fabrication and Properties of Lithium Ceramics III. Edited by I. J. Hastings and G. W. Hollenberg. Am. Ceram. Soc. Westerville, OH (1992).
[6] N. Balagopal Nair, T. Yamaguchi, H. Kawamura, and S. I. chiNakao, J. Am. Ceram. Sac. 87 (2004) 68.
[7] Q. Xiao, Y. Liu, Y. Zhong, and W. Zhu, J. Mater. Chem. 21 (2011) 3838.
[8] R. M. Wightman, L. J. May, and A. C. Michael, Anal. Chem. 60 (1988) 769A.
[9] K. R. Mahanthesha, B. E. Kumara Swamy, U. Chandra, S. Sharath Shankar, and K. V. Kumar Pai, J. Mol. Liq. 172 (2012) 119.

[10] S. Marceglia, G. Foffani, A. Bianchi, G. Baselli, F. Tamma, M. Egidi, and A. Priori, J. Physiol. 571 (2006) 579.
[11] S. Sharath Shankar, B. E. Kumara Swamy, U. Chandra, J. G. Manjunatha, and B. S. Sherigara, Int. J. Electrochem. Sci. 4 (2009) 592.
[12] N. Kemppainen, P. Marjamäki, M. Röyttä, and J. O. Rinne, J. Neural. Transm. 108 (2001) 827.
[13] Rekha, B. E. Kumara Swamy, R. Deepa, V. Krishna, O Gilbert, U Chandra, and B. S. Sherigara, Int. J. Electrochem. Sci.4 (2009) 832.
[14] S. Sharath Shankar, B. E. Kumara Swamy, U. Chandra, J. G. Manjunatha, and B. S. Sherigara, Int. J. Electrochem. Sci. 4 (2009) 592.
[15] C. Scheller, S. Sopper, C. Jassoy, V. terMeulen, P. Riederer, and E. Koutsilieri, J. Neural Transm. 107 (2000) 1483.
[16] J. Zheng, and X. Zhou, Bioelectroch. 70 (2007) 408.
[17] M. Zidan, T. W. Tee1, A. H. Abdullah, Z. Zainal, and G. J. Kheng, Int. J. Electrochem. Sci. 6 (2011) 289.
[18] J. K. Goh, W. T. Tan, F. T. Lim, and N. A. M. Maamor. Malaysian J. Anal. Sci. 12 (2008) 480.
[19] Z. Dursun, L. Pelit, and I. Taniguchi, Turk. J. Chem. 33 (2009) 223.
[20] L. Zhang, and X. Jiang, J. Electroanal. Chem. 583 (2005) 292.
[21] F. Arslan, Sensors 8 (2008) 5492.
[22] U. Chandra, B. E. Kumara Swamy, O. Gilbert, S. Reddy, and B. S. Sherigara, Am. J. Anal. Chem. 2 (2011) 262.
[23] J. S. Rodman, J. J. Williams, and C. M. Peterson, J. Urology 131 (1984) 1039.
[24] S. A. Wring, and J. P. Hart, Analyst 117 (1992) 1215.
[25] O. Gilbert, U. Chandra, B. E. Kumara Swamy, M. Panduranga Char, C. Nagaraj, and B. S. Sherigara., Int. J. Electrochem. Sci. 3 (2008) 1186.
[26] H. Jerabkova, K. Blanka, and J. Nahlik, Int. Biodeteriorat. 44 (1999) 233.
[27] J. Wang, B. Z. Zeng, C. Fang, and X. Y. Zhou, J. Electroanal. Chem. 484 (2000) 88.
[28] E. Niranjana, B. E. Kumara Swamy, R. RaghavendraNaik, B. S. Sherigara, and H. Jayadevappa, J. Electroanal. Chem. 631 (2009) 1.
[29] U. Chandra, B. E. Kumara.Swamy, O. Gilbert, and B. S. Sherigara, Int. J. Electrochem. Sci. 5 (2010) 1475.
[30] O. Gilbert, B. E. Kumara Swamy, U. Chandra, and B. S. Sherigara, Int. J. Electrochem. Sci.4 (2009) 582.
[31] K. C. Patil, M. S. Hegde, T. Rattan, and S. T. Aruna. World Scientific, Singapore. (2008) 292.
[32] H. N. Chandrakala, B. Ramaraj, Shivakumaraiah, G. M. Madhu, Siddaramaiah, J. Alloy. Compd. 551 (2013) 531.

[33] T. V. Sathisha, B. E. Kumara Swamy, S. Reddy, B. N. Chandrashekar, and B. Eswarappa, J. Mol. Liq. 172 (2012) 53.

[34] S. Reddy, B. E. Kumara Swamy, H. Jayadevappa, Electrochem. Acta 61 (2012) 78.

[35] S. Reddy, B. E. Kumara.Swamy, H. N. Vasan, and H. Jayadevappa, Anal. Met. 4 (2012) 2778.

[36] U. Chandra, B. E. Kumara. Swamy, O. Gilbert, S. Reddy, S. Shankar, M. T. Shreenivasa, and B. S. Sherigara, Anal. Met. 3 (2011) 2068.

[37] S. Reddy, B. E. Kumara Swamy, U. Chandra, K. R. Mahathesha, T. V. Sathisha, and H. Jayadevappa, Anal. Met. 3 (2011) 2792.